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RESEARCH MEMORANDUM

ORGANOPHOSPHORUS COMPOUNDS IN ROCKET-ENGINE APPLICATIONS

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Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
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SUMMARY

Experimental ignition-delay determinations of mixed alkyl thiophosphites, triethyl trithiophosphite, and propylene N,N-dimethylamidophosphite with red and white fuming nitric acids were conducted at temperatures from 140° to -95° F at sea-level pressure and at pressure altitudes of about 90,000 feet with a small-scale rocket engine of approximately 50 pounds thrust. Regardless of propellant combination or imposed temperature and pressure conditions, the ignition delays were all less than 10 milliseconds; most were in the range 1 to 6 milliseconds.

In addition, the literature pertaining to the use of organophosphorus compounds in rocket-propellant combinations was surveyed and summarized with particular emphasis on ignition-delay investigations.

The experimental data and literature survey were examined and evaluated with respect to utilization of organophosphorus compounds in rocket-engine applications. Although the exploitation of this new field of propellants is not complete, it appears that the tertiary compounds, especially thiophosphites and amidophosphites, are potentially outstanding rocket fuels since they meet proposed specifications better than many contemporary propellants and, if developed commercially, can assume excellent competitive positions with respect to other low-freezing-point, spontaneously ignitible fuels.

INTRODUCTION

In the search for liquid rocket fuels that are better than those now known and available, a useful guide is the set of target requirements formulated by the Bureau of Aeronautics (ref. 1 and table I). In addition to the items included in this list, another desirable goal is the discovery or development of self-igniting fuels that have very short delays over a wide range of temperatures with an extensively used oxidant such as fuming nitric acid. This characteristic is especially

desirable in applications where the total permissible propellant-burning time is extremely short and where ignition delay is a significant portion of this time.

In order to find fuels complying with the foregoing criteria, several investigators have examined and studied compounds outside the widely investigated classes such as alcohols, amines, and mercaptans (e.g., refs. 1 to 4). One such group that has received considerable attention recently is the large class of organophosphorus compounds. Several members of this class show promise not only as starting fuels but also as main fuels in certain applications. They possess many desirable chemical and physical properties as well as a potential for inexpensive, large-scale production.

As part of a general investigation conducted at the NACA Lewis laboratory on the suitability of certain fuels used with various nitric acids as self-igniting rocket propellant combinations (refs. 5 to 12), a literature survey of organophosphorus compounds pertinent to rocket applications was made and is reported in the appendix. In addition, ignition-delay determinations of three of the most promising ones, namely, mixed alkyl thiophosphites, triethyl trithiophosphite, and propylene N,N-dimethylamidophosphite, were made with red and white fuming nitric acids at temperatures from 140° to -95° F and at sea-level pressure and at pressure altitudes of about 90,000 feet with a small-scale rocket engine of approximately 50 pounds thrust and are also reported herein. The literature survey and the experimental results of the ignition-delay measurements are employed to evaluate the feasibility of these materials for further development.

APPARATUS

The ignition-delay apparatus utilized in the experimental investigation is shown diagrammatically in figure 1. It was a modification of the one reported in detail in reference 8. It also incorporated some of the features of a similar apparatus described in reference 11. The two major changes involved an improved propellant-injection system and a new means for assembling the rocket engine.

As shown in the insert of figure 1, the rocket-engine assembly consisted of an injector head, injector orifices, a transparent cylindrical combustion chamber, a plate with a convergent exhaust nozzle, and propellant tanks.

The internal geometric configuration was identical to the one in reference 8. The 90° included angle of the propellant streams, the center location of the combustion-chamber pressure tap in the injector head, the 0.68-inch propellant-stream travel before impingement, the

0.041-inch fuel-injector-hole diameter, the 4-inch-long and 2-inch-inside-diameter combustion chamber, and the 0.4-inch-throat-diameter exhaust nozzle were all unchanged. The 0.0675-inch-diameter oxidant injector was slightly larger than that used in reference 8.

The injector orifices differed from the earlier ones (ref. 8) in that they were not integral parts of the propellant tanks, but were separate injector-head inserts which were not removed during the course of the experiments. This system ensured production of propellant streams with invariant impingement characteristics. It also decreased experimental operating time by permitting simultaneous preloading of several pairs of propellant tanks.

The method for assembling the engine was modified by eliminating the connecting bolts between the injector head and the nozzle plate, and replacing this system by one in which the assembly was bound in compression between a rigid upper support and a movable lower screw-jack mechanism. Flexible metal bellows enclosed in the jack provided an air seal for the low-pressure experiments. These embodiments are shown in the cut-away view in figure 1.

PROCEDURE

The operating procedure employed in all experiments reported herein was essentially the same as the one described in reference 8. When a fast-acting solenoid valve was opened, pressurized helium burst sealing disks at each end of the propellant tanks and forced the propellants through injector orifices into the combustion chamber. Photographs were taken of the two propellant streams entering the combustion chamber, impinging, diffusing, and then igniting. Measurements of the ignition-delay period were made from the photographic data. As before, the propellant-injection pressure used in every run was 450 pounds per square inch gage.

PROPELLANTS

Fuels

Three organophosphorus fuels were used in this investigation. Two of them were derived from the class of thiophosphites: (1) a mixture of low-molecular-weight alkyl thiophosphites known as mixed alkyl thiophosphites and (2) triethyl trithiophosphite. The third was an amidophosphite, propylene N,N-dimethylamidophosphite. It is known more familiarly as 4-methyl-2-dimethylamino-1,3,2-dioxaphospholane.

The mixed alkyl thiophosphites was furnished by Standard Oil Company of Indiana. It was part of a particular pilot-plant quantity designated as Batch No. 6. An ultimate analysis and some physical properties of this specific batch are reported in reference 13. The over-all average molecular weight of this product is about the same as that of triethyl trithiophosphite.

The triethyl trithiophosphite was supplied by California Research Corporation and marked as Sample No. 53070-R.

The amidophosphite was provided by Shell Development Company. It was part of Lot No. P-3234. For brevity of nomenclature, Shell's coded designation for this fuel, RF 208, is widely used.

Each of these fuels was removed from its sealed container and immediately placed into smaller tightly enclosed ground-glass-stoppered bottles. The transfers were made with as little fuel-to-atmosphere contact as possible to minimize any hydrolytic or oxidative reactions that might occur.

Soon after initiation of the mixed alkyl thiophosphites program, it was observed that the 100-milliliter premeasured charges of fuel possessed cloudy appearances of various degrees. A yellowish sediment was also noted on the bottom of each bottle. Since the amount of material in each container was very slight, it was not known whether the solid contaminants were already present but unobserved at the time of receipt of the fuel or whether they were oxidation products that were formed in spite of the precautions taken to avoid them by rapid transfer and good sealing. Some of the clearest fuels were carefully decanted and results obtained with them were compared with those yielded by some of the cloudiest fuels that were thoroughly shaken before being transferred to propellant tanks. These tests disclosed no significant effects by the contaminants on ignition delay. In contrast to mixed alkyl thiophosphites, no visually observable amounts of settled or suspended sediment were ever found in the storage bottles of the other two fuels.

Some of the physical properties of the three fuels were determined and are as follows:

Fuel	Density, g/ml			Viscosity, centistokes		
	86° F	68° F	-40° F	77° F	-40° F	-65° F
Mixed alkyl thiophosphites	1.099	1.108	1.165	1.960	12.09	25.6
Triethyl trithiophosphite	1.095	1.104	1.157	1.880	10.61	21.4
Propylene N,N-dimethylamidophosphite	1.072	1.082	1.145	1.972	16.95	49.7

Freezing-point determinations were not successful because of the ready supercooling of the fuels to temperatures below -100° F.

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Oxidants

The two oxidants used in these ignition-delay studies were obtained as supernatant liquids from 55-gallon aluminum drums. The red fuming nitric acid (RFNA) contained approximately 3 percent water and about 20 percent nitrogen dioxide by weight. The white fuming nitric acid (WFNA) met USAF Specification No. 14104. Since the investigation was conducted over an extended period of time, an analysis was made of each batch removed from the drums and is included in table II, III, or IV.

RESULTS AND DISCUSSION

Mixed Alkyl Thiophosphites and Red Fuming Nitric Acid

Fifteen runs were conducted with mixed alkyl thiophosphites and red fuming nitric acid at temperatures from 120° to -93° F and at sea-level pressure and pressure altitudes of 82,500 and 90,000 feet. A summary of the data is presented in table II. A plot of ignition delay against average propellant temperature at various initial ambient pressures is shown in figure 2.

At sea-level pressure, the delays were essentially constant at about 3 milliseconds from 120° to -40° F. Below -40° F, they increased relatively rapidly until they reached almost 6 milliseconds at -95° F. The over-all increase in ignition delay was actually quite small, being only 3 milliseconds in a 200° F temperature interval. The short delays are in contrast with previously reported results obtained with a similar apparatus in which a comparatively slow-opening propellant-valve mechanism had been substituted for the quick-opening disk system (ref. 11). The delays in the former apparatus were about fourfold longer at corresponding temperatures which ranged from 80° to -70° F. The short delays at the very low temperatures (below -80° F) are contrary to results obtained with several open-cup apparatus (e.g., refs. 3 and 11), which indicate a sudden rise in ignition delay in that temperature region with various low-freezing-point acids. An explanation for the difference may be found in the relative insensitivity of the small-scale engine to viscosity effects (refs. 10 and 12).

At low initial ambient pressures and 120° F, the average ignition delay was slightly longer (about 2 millisec) than that obtained at sea-level pressure and the same temperature. At a pressure altitude of 90,000 feet and -93° F, the delay was essentially the same as at sea-level pressure and approximately the same temperature.

In accord with another reported observation (ref. 14), mixed alkyl thiophosphites and nitric acid gave smooth starts and left clean combustion chambers after reaction.

Triethyl Trithiophosphite and Red Fuming Nitric Acid

Eleven runs were made with triethyl trithiophosphite and red fuming nitric acid at temperatures from 121° to -95° F and at sea-level pressure and a pressure altitude of 90,000 feet. Table III presents a summary of the data. Ignition delay - temperature relations at various initial ambient pressures are plotted in figure 3.

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The ignition characteristics of this propellant combination were very similar to those exhibited by mixed alkyl thiophosphites and red fuming nitric acid, even with respect to actual values of ignition delay. At sea-level pressure, the average delays ranged from about 2.5 milliseconds at 120° F to almost 6 milliseconds at -95° F. At 121° F and a pressure altitude of 90,000 feet, the delay was 2 milliseconds longer than the one obtained at the same temperature but sea-level pressure. At low temperatures ($\leq$ -70° F), the delays at pressure altitudes of 90,000 feet were essentially the same as the delays at corresponding temperatures and sea-level pressure.

The similarities between triethyl trithiophosphite and mixed alkyl thiophosphites also extend to physical properties (e.g., densities, viscosities, freezing point), smooth starts, and clean combustion chambers.

Propylene N,N-dimethylamidophosphite and Red Fuming Nitric Acid

Eighteen runs were conducted with propylene N,N-dimethylamidophosphite and red fuming nitric acid at temperatures ranging from 132° to -93° F and at sea-level pressure and a pressure altitude of 90,000 feet. The experimental data and results are summarized in table IV. A plot of ignition delay - temperature relations at the two conditions of initial ambient pressure is presented in figure 4.

Ignition delays at sea-level pressure were less than 2 milliseconds at room temperatures and increased with decreasing temperature to about 8 milliseconds at -95° F.

In comparison with the two preceding fuels, the amidophosphite had shorter average delays at the higher temperatures, but longer average delays at the lower ones when red fuming nitric acid was the oxidant. The cross-over point may be placed somewhere between 0° and -15° F. Although the amidophosphite may have greater ignition reactivity than

either of the two thiophosphite fuels, its rapid rise in viscosity below -40° F appears to mask its reactivity to some extent by decreasing the mixing efficiency and thereby increasing the ignition delay.

As with the two preceding propellant combinations, the ignition delay at about 120° F and a pressure altitude of 90,000 feet was slightly longer than the average delay at the same temperature and sea-level pressure. At about -90° F, there was no significant difference between the delay at a pressure altitude of 90,000 feet and the average delay at sea-level pressure.

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In comparison with the thiophosphites, the amidophosphite also gave smooth starts; however, it left a heavy carbonaceous residue on the combustion-chamber walls after each run. The amount of deposit decreased with increasing initial temperature.

Mixed Alkyl Thiophosphites, Triethyl Trithiophosphite, and Propylene N,N-Dimethylamidophosphite with White Fuming Nitric Acid

Ignition-delay determinations of the three phosphite fuels were also conducted with white fuming nitric acid. Considerably fewer runs were made with this oxidant.

In the mixed alkyl thiophosphites - white fuming nitric acid series, the ignition delays, with one exception, ranged from an average of 5.5 milliseconds at 120° F to about 6 milliseconds at -40° F, regardless of initial ambient pressure (table II and fig. 5). The exception was a delay of 11.5 milliseconds at 115° F and sea-level pressure (run 261). No explanation can be offered for this anomaly at the present time.

The curve obtained with triethyl trithiophosphite was similar to the one yielded by mixed alkyl thiophosphites, but was lower by about 1/2 millisecond (table III and fig. 6). As with the latter fuel, the initial ambient pressure had no significant effect on ignition delay.

The amidophosphite - white fuming nitric acid curve was determined with more data than the preceding two (table IV and fig. 7). At sea-level pressure, the ignition delays ranged from about 2.5 milliseconds at 140° F to approximately 4 milliseconds at -40° F. At a pressure altitude of 90,000 feet, the delays at about 120° and -40° F were approximately the same as the corresponding sea-level values.

In comparison with results obtained with red fuming nitric acid, the thiophosphite fuels with white fuming nitric acid gave delays that were about 2 milliseconds longer over the comparable temperature range of 120° to -40° F. In a similar comparison, the amidophosphite yielded delays that were slightly longer at room temperatures but approximately the same between 20° and -40° F.

With respect to preignition characteristics with the amidophosphite, the red fuming nitric acid is probably more reactive than the white fuming acid; however, its greater viscosity seems to work to its disadvantage, especially at the lower temperatures, by producing poorer mixing and consequently longer delays. The same general trend is evident with the thiophosphite fuels although it is not as pronounced, possibly because of their higher fluidities at low temperatures.

As with red fuming nitric acid, the thiophosphites with white fuming acid left clean combustion chambers. In contrast, the amidophosphite produced carbonaceous residues with both oxidants. 3110

The ignition behavior of all three organophosphorus fuels with white fuming nitric acid is similar to that reported in the literature. In general, the actual delays are lower than published values for corresponding temperatures. A similar comparison between various laboratories cannot be made with these fuels and red fuming nitric acid since no experiments have been reported with comparable propellant combinations.

Discussion of Results at Subatmospheric Pressures

Ignition delays at low initial ambient pressures were not significantly different from those at sea-level pressure, particularly at low temperatures. The greatest effect of high altitude occurred with RFNA at 120° F where the ignition delay increased from 1 to 2 milliseconds. The effect of initial ambient pressure on ignition-delay results may be explained by a consideration of the liquid mixing of the oxidant and fuel jets. As discussed in reference 8, a propellant ejected into a rocket chamber at low initial pressures changes rapidly from a diffuse spray into a solid stream because of a pressure rise above its vapor pressure. The rise is caused by propellant evaporation and evolution of initial reaction gases. The rate of change depends on factors such as propellant flow rate, chamber size, and propellant vapor pressure. At 120° F, the vapor pressure of RFNA was high enough to show a noticeable increase in ignition delay. At lower temperatures, the vapor pressures were not sufficiently great to make an appreciable difference in ignition delay between high-altitude and sea-level conditions.

Since WFNA has a lower vapor pressure than RFNA (one-third less at 120° F), the effect of high altitude would be less with it than with RFNA; this premise was corroborated by the results.

SUMMARY OF RESULTS

Ignition-delay determinations of three organophosphorus fuels with nitric acid oxidants were made at simulated altitude conditions with a small-scale rocket engine of approximately 50 pounds thrust.

The results with low-freezing-point red fuming nitric acids containing approximately 3 percent water and 19 to 20 percent nitrogen dioxide by weight are summarized as follows:

1. With mixed alkyl thiophosphites at sea-level pressure, the ignition delays ranged from about 3 milliseconds at 120° F to approximately 6 milliseconds at -91° F. With the same propellant combination at pressure altitudes of about 90,000 feet, the delays were about 2 milliseconds longer at 120° F than comparable delays at sea-level pressure; however, this effect was not noted at the lower temperature limit.

2. With triethyl trithiophosphite at sea-level pressure and at a pressure altitude of 90,000 feet, the ignition delays from 120° to -95° F were generally similar to those produced by mixed alkyl thiophosphites and the same acid.

3. With propylene N,N-dimethylamidophosphite at sea-level pressure, the ignition delays varied from about 1.5 milliseconds at 130° F to 8 milliseconds at -93° F. With the same combination at a pressure altitude of 90,000 feet, the delay at 120° F was only slightly longer (about 1 millisec) than the corresponding delay at sea-level pressure. At -90° F, there was no significant difference at the two pressure conditions.

The results with white fuming nitric acids meeting USAF Specification No. 14104 are summarized as follows:

1. With mixed alkyl thiophosphites, the ignition delays, with one exception, ranged from an average of 5.5 milliseconds at 120° F to about 6 milliseconds at -40° F, regardless of initial ambient pressure.

2. With triethyl trithiophosphite, the ignition delay - temperature curve was similar to the one produced by mixed alkyl thiophosphites, but was lower by about 1/2 millisecond. The initial ambient pressure also had no significant effect on ignition delay.

3. With propylene N,N-dimethylamidophosphite at sea-level pressure, the ignition delays varied from about 2.5 milliseconds at 140° F to approximately 4 milliseconds at -40° F. At a pressure altitude of 90,000 feet, the delays at about 120° and -40° F were essentially the same as the corresponding sea-level values.

Smooth starts were observed with all six propellant combinations in all runs. No explosions occurred in any of the experiments.

Clean combustion chambers were always left by both thiophosphite fuels regardless of the oxidant used. With the amidophosphite and either fuming nitric acid, heavy carbonaceous residues were always deposited in the combustion chamber.

CONCLUDING REMARKS

In addition to the preceding experimental investigation, a survey of the literature pertaining to the use of organophosphorus compounds in rocket propellant combinations was made and is reported in the appendix. Both sources of information were utilized in obtaining a general evaluation of these compounds with respect to further development and in formulating specific suggestions for new and possibly potentially outstanding rocket fuels. The appraisal and recommendations are summarized as follows:

In general, trivalent organophosphorus compounds with low-molecular-weight alkyl substituents have excellent ignition characteristics with various nitric acid and hydrogen peroxide oxidants over a wide temperature range. Many of them possess desirable physical and chemical properties. Many are also compatible with ordinary materials of construction, have values of specific impulse over 200 pound-seconds per pound, are not very toxic, and have good potential logistic qualities, particularly in that they can be produced cheaply in large quantities from readily available raw materials. Members of all of the organophosphorus classes reported herein have been investigated as components of various fuel mixtures with encouraging results.

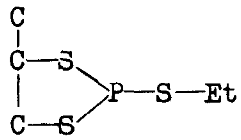
Among the disadvantages of some of these compounds is atmospheric instability due to either hydrolytic action or oxidation or both. Most of the compounds are also characterized by very disagreeable odors.

Amidophosphites and thiophosphites appear to be the outstanding classes investigated to date even though excessively corrosive reactions in the combustion chamber have been reported for some of them in engine-performance tests. The three fuels investigated experimentally and reported herein represent good examples of these classes but, in many respects, are certainly not the best obtainable. In the search for better propellants, however, they perform a valuable function by serving as well evaluated interim fuels until superior ones are developed and investigated.

Phosphonites seem to be the least attractive of all trivalent organophosphorus compounds.

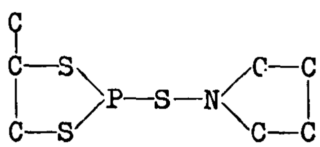
From the review of the literature, there is evidence that certain substituents, cyclic configurations, tertiary groupings, phosphorus-sulfur bonds, and phosphorus-nitrogen linkages contribute to the ignition reactivity of organophosphorus compounds. With this information, it is possible to make composites with these various structural components and produce compounds with exceptionally good rocket-fuel characteristics. A few examples of the many possibilities are as follows:

Ethylpropylene trithiophosphite



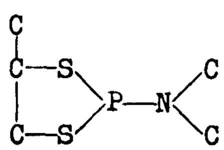
contains (1) the  configuration found to be strongly conducive to spontaneous ignition, as in triethyl trithiophosphite for example, (2) the general structure of the reactive tertiary cyclic phosphites, and (3) the methyl side chain that reduces the freezing point considerably under that of the ethylene compound. This compound will probably oxidize in air, but perhaps not as readily as triethyl trithiophosphite since two of the possibly influential sulfur atoms are tied up in a ring.

Pyrrolidylpropylene trithiophosphite



is similar to the preceding compound except that the ethyl radical is replaced by a pyrrolidyl ring which is known to have substantially improved the thermal stability of similar compounds. The higher molecular weight may detract somewhat from its performance.

Propylene N,N-dimethylamidodithiophosphite



eliminates one P—S linkage, but introduces the amido group which may be much more reactive. With no unrestricted phosphorus-sulfur bonds, this compound may be quite stable towards atmospheric oxidation.

Although many of the major groups of organophosphorus compounds have been investigated as sources for practical rocket fuels, there are still many other classes which have not been studied. Since this field of chemistry has already proved fruitful in the search for better rocket fuels, it may be advantageous to explore other promising groups such as the phosphinamides, phosphinimines, and phosphinites.

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Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
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APPENDIX - LITERATURE SURVEY

Introduction

Historical review. - Until recently, a large branch of organic chemistry, organophosphorus compounds, has been overlooked as a source of possible rocket fuels. At the present time, however, investigations into the organic chemistry of phosphorus are increasing very rapidly in many areas and its importance is becoming increasingly apparent. An inquiry into the possibility of its use in rocket fuels was inevitable.

The foundation of phosphorus chemistry as it is known today was laid by Carl A. Michaelis who emphasized the purely synthetic aspect. Many present references are attributed to Aleksandr E. Arbuzov, who is noted for his excellent experimental and theoretical contributions. Although the scientifically planned study of organophosphorus compounds is more than 100 years old, no over-all literature surveys or summaries were made until 1938, when Plets wrote his Organic Compounds of Phosphorus, a difficultly available book with Russian text. A more recent and complete treatment of the general aspects of the subject may be found in English in reference 15. A survey of the work of Michaelis and Arbuzov plus the information in reference 15 affords an investigator interested in new rocket fuels a good background review of this branch of chemistry.

In spite of the vast amount of literature being accumulated on organophosphorus compounds, adequate discussion of the reaction mechanisms of these substances is nonexistent. According to reference 15, the situation is due largely to a lack of any truly comprehensive studies along modern lines of such investigations.

An early reference to the reactivity of organophosphorus compounds with various substances may be found in a Russian article which describes the synthesis and properties of mixed thio esters of phosphorous acid (ref. 16). It is reported therein that these compounds are decomposed by water, alkalies, and strong acids. Nitric acid is especially vigorous and leads to explosive decomposition. It was also found, as is now well known, that all the esters are evil-smelling, unstable substances that are easily oxidized in air with the triethyl ester being especially sensitive to oxygen.

Nomenclature. - At the present time, there is no universally adopted system of nomenclature for organophosphorus compounds. Confusion exists because the same compounds are often given different names and, consequently, are assigned to different subgroups which have widely varying physical and chemical properties. Although the nomenclature in this report may be at variance with some of the systems used in the

various references that are cited, an attempt to establish uniformity has been made by keeping it in conformance with reference 15, which eliminates class names that may later become obsolete and which brings into closer relation several compound types that are set apart by current practices.

Classification. - Organophosphorus compounds may be subdivided as (1) phosphines, (2) halophosphines, (3) halophosphine halides, (4) phosphonyl halides, (5) quaternary phosphonium compounds, (6) tertiary phosphine oxides, sulfides, and selenides, (7) phosphinous, phosphonous, and phosphonic acids, and their esters, (8) phosphites, (9) halophosphites, (10) phosphates, (11) halophosphates, (12) compounds with phosphorus-nitrogen bonds, (13) quasi-phosphonium compounds, and (14) sulfur analogues of the oxygen-containing compounds. 3110

Many of the classes in this list have been investigated as sources for practical rocket fuels. To date, the most promising substances in the whole group are trivalent compounds among which certain amidophosphites and thiophosphites were found to be easy to prepare and to have very desirable chemical and physical properties as well as excellent ignition qualities. These particular classes will be emphasized herein.

Phosphines

General review. - Phosphines were among the first of the organophosphorus compounds to be investigated as possible rocket fuels. They are very reactive substances, as are all derivatives of trivalent phosphorus (ref. 15). As a class, they possess the unpleasant characteristic odor of phosphine and are somewhat toxic.

Although all phosphines are subject to oxidation, primary and secondary phosphines (especially those containing lower aliphatic radicals) are outstanding in their affinity for atmospheric oxygen. The aromatic derivatives, especially the tertiary forms, are rather stable in this respect, but are readily attacked by various oxidizing agents (ref. 15).

Alkyl phosphines: Alkyl phosphines can be produced by the reaction of olefins with phosphine, an attractive and feasible method for converting hydrocarbons to hypergolic fuels (spontaneously ignitible with an oxidant) on a commercially large scale (ref. 17). They can also be prepared by the reaction of phosphorus trichloride with the corresponding Grignard reagent (refs. 1 and 3).

In qualitative open-cup ignition tests at 75° F, various primary phosphines (2-ethylhexyl, *n*-octyl, and dodecyl) and a secondary phosphine (di-2-ethylhexyl) had excellent ignition properties with various nitric acid type oxidants: WFNA (probably 98 percent HNO_3), RFNA (22 percent NO_2), WFNA (90 percent HNO_3), and nitrogen tetroxide (N_2O_4) (refs. 3 and 18). These particular phosphines could be diluted with *n*-heptane to 40 to 60 percent of the total volume and still remain hypergolic with WFNA (98 percent HNO_3) and N_2O_4. In this respect, the branched phosphines were better than the straight-chain compounds. In another open-cup apparatus (refs. 3 and 18), the same primary compounds had ignition delays of 4 to 10 milliseconds at 75° and -40° F with WFNA (probably 98 percent HNO_3). In the qualitative open-cup apparatus of reference 17, certain tertiary phosphines (trimethyl, tri-*n*-butyl, and tri-*sec*-butyl) were found to be much less reactive than the primary or secondary compounds (refs. 3 and 18). The tri-*n*-butyl compound was nonhypergolic under the particular test conditions. Another investigator found tri-*n*-propylphosphine to be very reactive with WFNA ($>$ 95 percent HNO_3) at room temperature but completely unsatisfactory in reactivity at -40° F (ref. 1).

Alkyl phosphines have also been investigated with hydrogen peroxide (H_2O_2) as the oxidant. A summary of the results obtained with an open-cup ignition apparatus with neat compounds and some benzene blends is shown in table V (refs. 18 and 19). The data indicate that alkyl phosphines in general have good ignition qualities with hydrogen peroxide oxidants (80 percent and 90 percent H_2O_2) as compared to the reactivity of other hypergolic fuels with these oxidants. The primary phosphines appear to be slightly superior to the secondary and tertiary compounds. As a consequence, the limiting dilution with benzene is less with the tertiary phosphines than with the primary compounds.

Aryl phosphines: Aryl phosphines have been studied with various nitric acid oxidants. Phenylphosphine ignited very rapidly with WFNA (90 percent HNO_3) (refs. 20 and 21), WFNA ($>$95 percent HNO_3) (ref. 22), and a mixed acid (ref. 21) in qualitative open-cup ignition tests at room temperature and at -40° F. Quantitative open-cup ignition experiments with 90 percent nitric acid yielded ignition delays ranging from about 7 milliseconds at 70° F to about 15 milliseconds at -65° F (ref. 21). Although phenylphosphine is very reactive, it is not very practical as a fuel in the unblended form because it reacts spontaneously with air, and its combustion products are extremely toxic (ref. 20).

The usefulness of phenylphosphine as a blending agent has been investigated. It was tried as an additive to jet fuel (JP-3), but, of the total volume, 30 percent phenylphosphine was necessary to make the

blend hypergolic (refs. 20 and 21). It was also added to 2-methyl-1-buten-3-yne in an attempt to improve the ignition qualities of this material, especially at low temperatures. With white fuming nitric acids (90 percent and >95 percent HNO_3), a substantial improvement was obtained with 25 percent additive both at room temperature and at -40° F (refs. 21 and 22). With mixed acid, the improvement was not satisfactory at -40° F (ref. 21).

Economics. - A preliminary study of the cost and availability of alkyl phosphines is reported in references 3 and 18. Although no commercial sources of the important raw material, phosphine, exist at the present time because of a lack of demand, it should be possible to produce the compound relatively cheaply since large quantities of hydrogen and phosphorus are available at low cost. Because phosphine reacts with olefins in the C_6 to C_{12} range in 80 to 90 percent yields, it is estimated that the corresponding alkyl phosphines can be produced at less than 30 to 35 cents per pound. Branched alkenes are more easily available than straight-chain olefins; this is fortunate since phosphines derived from the former have lower, and therefore more desirable, freezing points than those obtained from the latter.

Summary. - Phosphines are very reactive substances, but this desirable quality is somewhat offset by their unpleasant odor and toxicity. Although the primary and secondary compounds are outstanding among the alkyl phosphines from the standpoint of ignition with various nitric acid and hydrogen peroxide oxidants, they are among the most unstable of all the phosphines in air. Aryl phosphines also possess satisfactory ignition delays with nitric acid oxidants. In general, phosphines can be diluted to a considerable extent with various hydrocarbons and still remain hypergolic. Alkyl phosphines are potentially available in large quantities and at low cost.

Halophosphines

General review. - The investigation of halophosphines as possible rocket fuels has been limited to probably one compound, ethyldichlorophosphine. Study of its ignition behavior has been confined to hydrogen peroxide oxidants (ref. 3). It is exceedingly hypergolic with 90 percent H_2O_2 and is even self-igniting with 60 percent H_2O_2. Excellent ignition properties at low temperatures are obtained with H_2O_2 solutions of NH_4NO_3.

At room temperature, blends of ethyldichlorophosphine and toluene to at least a 1:1 mixture by volume are hypergolic with 90 percent H_2O_2. Blends with lesser amounts of toluene are self-igniting with

80 percent H_2O_2 to -2° F and with H_2O_2-NH_4NO_3 mixtures to -42° F (ref. 3).

Summary. - Probably only one halophosphine has been examined for possible rocket applications. The excellent ignition properties of the compound, ethyldichlorophosphine, and various hydrocarbon blends with hydrogen peroxide as oxidant indicate a need for further exploitation of this group.

Phosphites

General review. - The phosphites that have been of interest in rocket applications are esters of phosphorous acid. Primary phosphites are generally sirups that show monobasic properties and are very resistant to oxidation (ref. 15). They may be regarded as existing in the free state in the form of the keto structure, ROP(O)(OH)H, with only one normally ionic hydrogen. It is probably because of these characteristics that they have not received serious consideration for use as rocket fuels.

The secondary esters are essentially odorless liquids that can be distilled in vacuo. Their lack of oxidizability is explained by the fact that, in the free state, they exist substantially in the keto form instead of the $(RO)_2P(OH)$ form. Raman spectra and parachor measurements for molecular structure determination show further that the substances exist in the free state in the form of associated, probably cyclic, configurations that may be assigned dimer or trimer magnitudes (ref. 15).

The tertiary esters are possibly the most reactive substances in this class (ref. 15), and, consequently, have received the greatest attention in the rocket field. In contrast to the other two groups, these compounds are true derivatives of trivalent phosphorus and, as such, they undergo the usual addition reactions including oxidation to the corresponding phosphate. Trialkyl phosphites are oxidized rather slowly to the corresponding phosphates by contact with atmospheric oxygen (ref. 22). This stability is advantageous in situations where long-term storage is often a serious problem. Tertiary esters in which two of the phosphorus valences are ester-bound by a cyclic structure (from glycol esterification) are known and have been examined for rocket applications.

Phosphites serve as useful intermediates for synthesis of numerous organophosphorus compounds. In addition to this transient utility, the tertiary esters have found fairly extensive use as antioxidants, particularly in the field of oil additives (ref. 15).

Phosphites that have been investigated as possible rocket fuels may be divided into two categories: acyclic and cyclic. This particular separation differentiates them quite sharply with respect to ignition characteristics.

Acyclic phosphites: In the acyclic group, dialkyl phosphites were found to have poor ignition qualities. Sodium diethyl phosphite in toluene (30 percent by weight) and diethyl phosphite would not ignite in an open-cup ignition apparatus at room temperature or -40° F with either WFNA (> 95 percent HNO_3) or a mixed acid (ref. 22). Paraffinic, olefinic, and acetylenic tertiary compounds were also tested in the same 3110 apparatus. There is no apparent correlation among their ignition reactivities. With WFNA (90 percent HNO_3) and various mixed acids, trimethyl and tripropargyl phosphites ignited satisfactorily at room temperature (ref. 21), whereas the triethyl (ref. 24) and triallyl compounds (ref. 21) yielded unacceptable delays (> 1 sec to ∞). At -40° F, however, no ignition was possible except with trimethyl phosphite and WFNA (90 percent HNO_3) (ref. 21). With WFNA (> 95 percent HNO_3), the same tertiary compounds with the exception of the triple-bonded one had excellent ignition characteristics at room temperature (ref. 22); the latter did not ignite. At -40° F, the trimethyl compound was again the only one that would ignite.

Cyclic phosphites: In the cyclic group of phosphites in which the phosphorus is in a ring system, only tertiary compounds have been investigated. In contrast to the acyclic phosphites, the cyclic compounds possess considerably greater ignition activity. Various compounds tested in an open-cup ignition apparatus with several nitric acid oxidants all had good ignition properties at room temperature and in general had similar characteristics at -40° F (refs. 1, 21, 22, and 24). A summary of the results of these experiments is shown in table VI. In similar tests, one of the compounds, ethyltrimethylene phosphite, ignited vigorously with H_2O_2 (90 percent) at room temperature and -40° F (ref. 1). Another one of the compounds, methylethylene phosphite, yielded ignition delays of 20 milliseconds at 68° F and 40 milliseconds at -40° F with WFNA (> 95 percent HNO_3) in another ignition apparatus (ref. 1). In this apparatus and with the same acid, ethyltrimethylene phosphite gave a delay of 50 milliseconds at -40° F (ref. 1).

One undesirable chemical property generally possessed by these cyclic phosphites is the ring opening obtained upon hydrolytic treatment (ref. 15). It usually takes place quite vigorously.

Cyclic phosphite blends: The reactivity of these cyclic compounds suggested their use as blending agents for inducing or enhancing hypergolic action of a fuel that is desirable in other respects. Neither

2-methyl-1-buten-3-yne (ref. 21) nor JP-3 (ref. 1) are hypergolic with mixed acids at -40° F; however, good ignition characteristics were obtained with solutions of these compounds containing 25 percent by volume of propargylpropylene phosphite. The effects of the additive decrease rapidly with decreasing concentration. A similar amount of the same phosphite in the alkenyne did not make it hypergolic with WFNA (90 percent HNO_3) (ref. 21). Although methylethylene phosphite seems to be more reactive than the propargyl compound according to table VI, 25 percent by volume of it in the same alkenyne could not produce spontaneous ignition when mixed with WFNA ($>$ 95 percent HNO_3) at either room temperature or -40° F (ref. 1).

Summary. - The most reactive phosphites are the tertiary esters. Of these, the cyclic compounds possess the greatest ignition reactivity. Although the latter may be satisfactory for certain rocket applications, they generally suffer ring opening on hydrolytic treatment and, therefore, serve a much better purpose by acting as intermediates for synthesis of other organophosphorus compounds.

Halophosphites

General review. - Halophosphites may be regarded as ester halides of the parent phosphorous acid. They are usually liquids which resemble the trichloride in their general appearance and behavior (ref. 15). Since the trihalides are similar to the halophosphites and since they may be regarded as phosphites in which all three of the (OR) groups have been replaced by halogen, these compounds will also be included in this section.

Primary dihalophosphites are usually very stable to heat, with the chloro derivatives being best in this respect (ref. 25). On the contrary, the secondary monohalophosphites are usually unstable thermally and in prolonged storage (ref. 15). As phosphites, halophosphites serve as useful intermediates for the synthesis of many organophosphorus compounds.

Cyclic halophosphites: Excluding the phosphorus trihalides, cyclic secondary monohalophosphites are probably the only halophosphites that have been investigated as rocket fuels to the present time. In a qualitative open-cup apparatus, ethylene chlorophosphite had excellent ignition characteristics with WFNA ($>$ 95 percent HNO_3) and a mixed acid at room temperature and -40° F (ref. 22). The ignition reactivity of propylene chlorophosphite tested under the same conditions was almost as good (refs. 21, 22, and 24). This compound also ignited satisfactorily with WFNA (90 percent HNO_3) at the same temperatures (ref. 24).

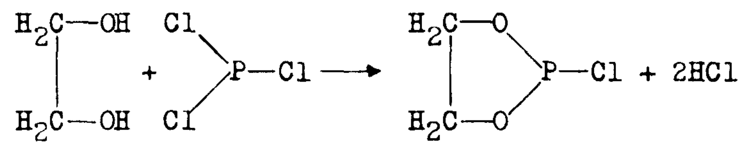
Trimethylene chlorophosphite ignited very rapidly with WFNA (> 95 percent HNO_3) and hydrogen peroxide (90 percent) at room temperature and -40° F (ref. 1). In quantitative open-cup ignition apparatus, ethylene, trimethylene, and propylene chlorophosphites with WFNA (> 95 percent HNO_3) yielded delays of 23 milliseconds (refs. 1 and 22), 17 milliseconds (ref. 1), and 29 milliseconds (ref. 1), respectively, at -40° F. The ethylene compound was also tested with the same acid at other temperatures, yielding delays of about 15 to 23 milliseconds at 68° to 70° F (refs. 1 and 22) and about 25 milliseconds at -70° F (ref. 22). Another laboratory reports a delay of only 9 milliseconds at -70° F for the propylene ester and WFNA containing approximately 4 percent water and 4 percent sodium nitrite (ref. 26). 3110

Ethylene chlorophosphite has been utilized as an ignition-upgrading blending agent. A solution of this compound in 2-methyl-1-buten-3-yne (25 percent by volume) reduced the ignition delay of the latter with WFNA (> 95 percent HNO_3) to 15 milliseconds at room temperature (ref. 22). At -40° F, however, the delays were long (about 130 millisec) and erratic.

A major drawback in the use of halophosphites as rocket fuels is the hydrolysis of most of the compounds. Water reacts with halophosphites to form the corresponding phosphites (primary or secondary). Propylene chlorophosphite, for example, is chemically unstable when exposed to a humid atmosphere (ref. 26).

Phosphorus trihalides: Phosphorus trihalides have been tested with both nitric acid oxidants and hydrogen peroxide. In experiments at 70° and -40° F in a modified open-cup apparatus, the trichloride did not ignite with either WFNA (98 percent HNO_3) or RFNA (8 percent NO_2) (ref. 11). Another laboratory advanced the hypothesis that compounds containing a phosphorus-halogen bond are extremely reactive towards hydrogen peroxide (refs. 18 and 19). It was supported in part by the fact that PBr_3 and PCl_3 are both hypergolic with H_2O_2 (90 percent). The trichloride was less reactive than the tribromide (ref. 19) and had a long delay of 14 seconds at room temperature (ref. 18). It has also been shown that fuels containing small amounts of phosphorus halides are improved with respect to self-igniting qualities with hydrogen peroxide (ref. 3).

Economics. - Cyclic phosphites of the type discussed in this section have been known for a long time, but could not be prepared in high yields until recently (ref. 27). Ethylene chlorophosphite, for example, has been produced in essentially quantitative yields according to the following equation (ref. 1):



ethylene glycol	phosphorus trichloride	ethylene chloro-phosphite	hydrogen chloride

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In turn, this chloride has been reacted with alcohols, mercaptans, and amines in good yields (ref. 1). With relatively cheap raw materials that are readily available, these compounds can be produced potentially in large amounts at low cost.

Summary. - Excluding the phosphorus trihalides, cyclic secondary monohalophosphites are probably the only halophosphites that have been investigated as possible rocket fuels to the present time. Although these particular compounds all have excellent ignition characteristics and can be produced potentially in large amounts at low cost, they have the disadvantage of being chemically unstable in contact with water. They serve a useful purpose, however, as intermediates in the synthesis of other, more stable organophosphorus rocket propellants.

Amidophosphites and Amidohalophosphites

General review. - The rocket fuels discussed in this section are amides of phosphorous acid esters and halides, and blends of these substances with various hydrocarbons and other compounds. A summary of the results obtained with an open-cup ignition apparatus for several neat members of this group with hydrogen peroxide and several nitric acid oxidants at room temperature and at -40° F is given by table VII. In general, these compounds have excellent ignition characteristics. The few fuels which were rated lower than "10" (table VII) either had no N-alkyl substitutions or contained alkyl substituents with more than two carbon atoms. Of interest is the monochloro compound, N, N, N', N'-tetramethyldiamidochlorophosphite, which bursts into flame when poured into water (ref. 1).

In another open-cup apparatus, one of the acyclic triamides, N,N,N',N',N",N"-hexamethyltriamidophosphite, was hypergolic at -78° F with a low-freezing-point white fuming nitric acid containing 4 percent KNO_3 and 4 percent H_2O (ref. 28). This fuel, as well as its hexaethyl homologue, was self-igniting even with WFNA (70 percent HNO_3), presumably at room temperature (ref. 28). The latter fuel was crude, probably containing N,N,N',N'-tetramethyldiamidochlorophosphite. It was extremely reactive, being hypergolic with 80 percent H_2O_2 at -20° F (ref. 19).

Preliminary drop tests of various distillation fractions of two relatively new fuels (di-n-propyl N,N-dimethylamidophosphite and di-n-propyl N,N-di-n-butylamidophosphite) with WFNA (> 95 percent HNO_3) generally gave excellent ignitions (ref. 29). The evaluation of these compounds as rocket propellants is in progress (ref. 29).

Actual values of ignition delay for many of these compounds have been obtained with various open-cup ignition apparatus and are listed in table VIII. In this group, the fuel with the shortest delay is a cyclic compound, ethylene N-methylamidophosphite. With WFNA (> 95 percent HNO_3), it yielded a delay of only 6 milliseconds at -40° F. All halophosphites listed in this table react with water. One of them, N,N,N'-trimethyldiamidochlorophosphite, actually ignites when poured into water. In the subgroup of cyclic amidophosphites, the propylene compounds are more desirable than the corresponding ethylene homologues since the side-chain methyl group reduces the freezing point considerably without appreciably affecting the other important properties. It was also found that the addition of a pyrrolidyl ring substantially improves high-temperature stability. In reference 30 the most thermally stable material tested was a phosphorous triamide with a pyrrolidyl ring.

Small-scale rocket engines have also been used to measure ignition delays of amidophosphites. With an engine of 50 pounds thrust, propylene N,N-dimethylamidophosphite gave delays of 12 and 14 milliseconds with RFNA (11.4 percent NO_2) and WFNA (2.4 percent NO_2), respectively, (ref. 31). The experiments were probably made at room temperature.

Operational screening tests in a 70-pound-thrust rocket engine at 300 pounds per square inch absolute chamber pressure have been conducted with propylene N,N-dimethylamidophosphite and WFNA (ref. 14). With an acid lead and various oxidant-fuel ratios, extremely smooth starts and clean, stable combustion were obtained. A maximum specific impulse of 182 pound-seconds per pound at an O/F of 2.0 was only 81 percent of theoretical. The runs were characterized by excessive corrosive action in the combustion chamber, particularly in the nozzle section.

Amidophosphite blends: Because of their reactivity, amidophosphites have been studied extensively as blending agents. Many of the compounds listed in tables VII and VIII as well as others reported only in blends, such as ethylene N,N-di-2-ethylhexylamidophosphite, have been utilized to enhance the ignition characteristics of two acetylenic hydrocarbons, 2-methyl-1-buten-3-yne and 1,6-heptadiyne, both of which are attractive from the standpoint of potential availability and low cost (refs. 1, 4, 21, 22, 30, and 32). Ignition experiments were also conducted with mixtures of amidophosphites and other hydrocarbons such as JP-3, isooctane, n-heptane, and toluene (refs. 1, 4, and 30). A few blends of

amidophosphites with one another have been investigated (refs. 32). Some tests were also conducted with an acetylenic amine-triamide mixture (ref. 1). In many cases, performance characteristics, physical properties, storability, thermal stability, toxicity, and mechanical shock stability of these mixtures are reported along with the ignition characteristics in the same references. In general, the triamides are the most effective ignition upgraders. In this subgroup, N,N',N"-trimethyltriamidophosphite is outstanding in this respect (ref. 4).

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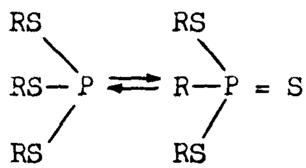
Economics. - If produced in quantities of 50,000,000 pounds per year, any one of the preceding desirable amidophosphites can be manufactured to compete with prevailing hypergolic rocket fuels. Based on satisfactory physical properties, good performance, and short ignition delays with WFNA, one of these compounds, propylene N,N-dimethylamidophosphite, was chosen for a more extensive, as well as intensive, investigation. Its toxicity, corrosiveness, storage stability, thermal stability, impact stability, and compatibility with containing substances were reported as being satisfactory (refs. 30 and 33). It can be made from starting materials that are readily available in commercial quantities with a cost of about 35 cents per pound. Production has already reached the pilot-plant stage (ref. 33).

Summary. - In general, amidophosphites with N-alkyl substituents and small alkyl radicals have excellent ignition characteristics. In addition, many of them meet most of the Bureau of Aeronautics target requirements for rocket fuels. Although limited engine tests indicate extremely smooth starts and clean, stable combustion with these compounds, some trouble may be encountered with excessive corrosive action in the combustion chamber. Because of their reactivity, amidophosphites have been studied extensively as fuel blending agents. The triamides appear to be the most effective ignition upgraders.

Except for hydrolytic reactivity, amidohalophosphites possess the same desirable qualities as the amidophosphites.

Thiophosphites, Halothiophosphites, and Amidothiophosphites

General review. - The rocket fuels discussed in this section are esters, ester halides, and amides of thiophosphorous acids. The esters may be prepared by the reaction of phosphorus trichloride with a mercaptan (ref. 34) or by the reaction of yellow phosphorus with alkyl disulfides (ref. 35). The latter process is more desirable because the procedure is simpler, the yield is much higher, and the product has a narrower boiling range (ref. 3). Also, the raw materials are potentially available at a low cost. Infrared analyses identify P=S bonds in products obtained by both methods and indicate the following possible equilibrium (ref. 28):



A similar reaction is known for the oxygen analogue.

In addition to their usefulness as rocket fuels, thiophosphorous acid esters are good extreme-pressure-lubricant additives (ref. 36). 3110 Triethyl trithiophosphite by itself is a better lubricant than conventional petroleum oils, but it is not as effective as extreme pressure lubricants themselves (ref. 37). Since most liquid lubricants used in rocket hardware are dissolved by thiophosphites, the latter can replace them and perform their functions in certain applications (ref. 37).

Triethyl trithiophosphite: As a group, thiophosphites have not been investigated as extensively as some of the others with respect to total number surveyed; however, one of its tertiary members, triethyl trithiophosphite, has probably been studied as a possible rocket fuel by more laboratories than any of the other organophosphorus compounds. Blends of this ester with various hydrocarbons have received a comparable amount of attention. In addition to its desirable physical properties and short ignition delays with nitric acid oxidants, one of the reasons for its wide investigation is its selection as a reference fuel in an ignition-delay-apparatus standardization program formulated during a conference on "Rocket Fuels Derivable from Petroleum" held in San Francisco in March, 1952. Eleven organizations participated in this program. The results of their tests are summarized in reference 38. In addition, several of the participants released separate reports of all or portions of their data (e.g., refs. 3, 11, 31, 39, and 40). Open-cup and small-scale rocket engine apparatus were both used in the investigation. The experiments were conducted at 75° , 32° , and -40° F with WFNA (> 98 percent HNO_3) and triethyl trithiophosphite blends containing 0, 10, 20, 30, and 40 percent by volume of n-heptane. In many instances, the results for the same conditions varied by a whole order of magnitude between the various organizations. At each test temperature, the lowest average values were less than 10 milliseconds for the neat compound. The delays generally increased with an increase in the amount of diluent. The reported effects of temperature, however, were inconsistent; there was either an increase, a decrease, or no change in ignition delay with a decrease in temperature. At the extreme conditions of -40° F and 40 percent n-heptane, the lowest average delay was 32 milliseconds. In addition to the different methods used for determining ignition delay, part of the variance in results may be attributed to the extent of oxidation of the fuel at the time of experiment.

Triethyl trithiophosphite has been tested with various other nitric acid oxidants. With WFNA containing 4 percent water and 4 percent sodium nitrite, it yielded an ignition delay of 17 milliseconds at -70° F (refs. 26 and 40). With a similar oxidant, the delay was 11 milliseconds at -70° F (ref. 26). With a blend of anhydrous WFNA (85 percent by volume) and methane sulfonic acid (15 percent by volume), the delay was only 8 milliseconds at the same temperature (ref. 41). It also ignited with N_2O_4 and H_2O_2 in an open-cup apparatus; however, there was a long delay with the latter oxidant (ref. 41).

Trimethyl trithiophosphite and other homologues: Some of the homologues of triethyl trithiophosphite have also been investigated. Trimethyl trithiophosphite is reportedly more reactive than the triethyl ester (ref. 28). At room temperature, it yielded very short delays with WFNA (probably 97 percent HNO_3) and WFNA containing 4 percent H_2O and 4 percent KNO_3 (ref. 28). At low temperatures (< -70° F), the delays were still very short. An ester product prepared from methylethyl disulfide gave similar results (ref. 28). Another laboratory reported a delay of only 6 milliseconds at -70° F for the trimethyl ester and a low-freezing-point WFNA containing sodium nitrite (ref. 26). This is 5 milliseconds less than that obtained with the triethyl ester under the same conditions (ref. 26) and is in accord with reference 28 with respect to the order of relative reactivity between these two compounds. Hypergolic activity decreases with increasing size of the alkyl groups (ref. 28). Tri-n-propyl and tri-n-butyl trithiophosphites have poor ignition characteristics. The same relative ignition relations among these homologues exist with 90 percent H_2O_2 (ref. 18).

Mixed alkyl thiophosphites: There is a considerable amount of interest in a fuel known as mixed alkyl thiophosphites which has an over-all average molecular weight about equal to that of triethyl trithiophosphite. Its ignition properties are also similar to those of the triethyl ester (refs. 17, 18, 26, 30, and 42). Delays of less than 10 milliseconds with WFNA (> 97 percent HNO_3) at room temperature have been reported in an open-cup apparatus (ref. 11) and a small-scale rocket engine (ref. 39). Another investigator compared this fuel and WFNA containing 4 percent H_2O and 4 percent $NaNO_2$ with triethyl trithiophosphite and the same oxidant with the following results (ref. 26):

Fuel	Average ignition delay, millisec	
	-40° F	-70° F
Mixed alkyl thiophosphites	8	27
Triethyl trithiophosphite	9	17

The effect of temperature on the ignition delay of mixed alkyl thiophosphites with low-freezing-point blends of WFNA and various nitroparaffins is reported in reference 3. The addition of nitroparaffin to acid increased ignition delay only slightly at room temperature and considerably at -40° F. This fuel has also been tested with 90 percent H_2O_2, probably at room temperature (ref. 3). An unsatisfactory delay of 75 milliseconds resulted.

Engine experiments: Tests with WFNA and trimethyl and triethyl trithiophosphites have been conducted in a rocket engine of 220 pounds thrust (ref. 26). With both fuels, starting was smooth, but the specific impulses were lower and the exhaust products were smokier than those obtained with mixed butyl mercaptans. Similar results were obtained with the triethyl ester and with mixed alkyl thiophosphites in a smaller engine of 70 pounds thrust (ref. 14). Stable combustion was obtained over the entire range of oxidant-fuel ratios used in the tests. Values of maximum specific impulse were far below theoretical values as shown in the following table; however, these performance figures should be considered as qualitative since an optimum test vehicle was not used.

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Fuel	Theoretical performance, frozen equilibrium		Experimental performance		Percent of theoretical
	Maximum specific impulse, lb-sec/lb	Oxidant-fuel ratio	Maximum specific impulse, lb-sec/lb	Oxidant-fuel ratio	
Triethyl trithiophosphite	196	2.9	180	2.3	92
Mixed alkyl thiophosphites	213	2.4	186	2.6	87

In these tests, the combustion products were found to be extremely corrosive to the stainless-steel chambers and nozzles at the engine operating temperatures and pressures. The combustion chamber had a clean scrubbed appearance after each test.

Alkyl thiophosphite blends: Both mixed alkyl thiophosphites and triethyl trithiophosphite have been blended with various hydrocarbons. Some studies have been conducted with alkyne mixtures and WFNA; the results are shown in the following table:

Fuel	Diluent	Amount of diluent, percent by volume	Ignition delay, millisec			Reference
			WFNA (90-percent HNO_3)	WFNA (> 95-percent HNO_3)		
			-40° F	Room temperature	-40° F	
Mixed alkyl thiophosphites	2-Methyl-1-buten-3-yne	50	80	--	40	30
Mixed alkyl thiophosphites	1,6-Heptadiyne	50	No ignition	--	No ignition	30
Triethyl trithiophosphite	2-Methyl-1-buten-3-yne	75	--	65	170	1, 22
Triethyl trithiophosphite	1,6-Heptadiyne	50	--	--	No ignition	4, 43

Mixed alkyl thiophosphites blends with n-heptane, diisobutylene, and toluene have also been reported (ref. 18); but, because of faulty instrumentation, the values of ignition delay were later questioned (ref. 3).

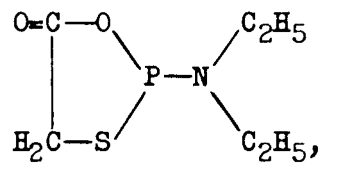
A 1:1 blend of triethyl trithiophosphite and n-heptane failed to ignite at -70° F with an 85:15 blend of anhydrous WFNA and methane sulfonic acid (ref. 2). Various mixtures of triethyl trithiophosphite and the ethyl mercaptal of acetaldehyde yielded short delays at -70° F with a blend of anhydrous WFNA and methane sulfonic acid; however, none of the fuel blends had a delay as short as the 8 milliseconds given by the neat thiophosphite (ref. 41).

Blends of trimethyl trithiophosphite with unsaturated hydrocarbons have been investigated as a means of decreasing the low-temperature viscosity and the freezing point of the phosphorus compound (ref. 29). A summary of the data is given in table IX. As shown by the table, blends containing from 0 to 40 volume percent hydrocarbon generally have excellent delays at -65° F. Dilution studies of the trimethyl ester with benzene have been made with 80 percent and 90 percent H_2O_2 as oxidants (ref. 3). As little as 30 percent by volume of thiophosphite in benzene is hypergolic with 90 percent H_2O_2 at room temperature.

Cyclic thiophosphites: Some cyclic thiophosphites in which sulfur is not in the ring with phosphorus have been studied. S-ethylethylene thiophosphite (2-ethylmercapto-1,3,2-dioxaphospholane) and S-ethylpropylene thiophosphite (4-methyl-2-ethylmercapto-1,3,2-dioxaphospholane)

would not ignite properly with either WFNA (> 95 percent HNO_3), or 90-percent H_2O_2 (ref. 1). These results are in contrast to those obtained with the oxygen homologues (see section on Phosphites).

An unnamed cyclic thiophosphite,



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in which sulfur and phosphorus are in the same ring was tested with WFNA containing 4 percent H_2O and 4 percent $NaNO_2$. From the structure, the substance could possibly be called S,O-ethionylene N,N-diethylamidothiophosphite or 4-oxy-2-diethylamino-1-thia-3-oxa-2-phospholane. At 72° and 0° F, ignition delays of 10 and 60 milliseconds, respectively, were obtained (ref. 2). Its difficult preparation and long ignition delay at 0° F eliminated this compound from further consideration as a rocket fuel.

Aryl thiophosphites: An aromatic compound, tritolyl trithiophosphite, has been prepared in good yield; however, it was not studied extensively because of its poor ignition qualities (ref. 3).

Halothiophosphites: Only a small amount of work has been done with halothiophosphites. Diethyl chlorodithiophosphite is hypergolic with 90-percent H_2O_2 at room temperature (ref. 18). Ethyl dichlorothiophosphite has an ignition delay of 50 milliseconds at -70° F with WFNA containing approximately 4 percent water and 4 percent sodium nitrite (ref. 26). This is considerably greater than the < 20 milliseconds yielded by triethyl trithiophosphite with the same oxidant in the same apparatus. Both of the halophosphites were hypergolic with 80-percent H_2O_2 containing 30-percent NH_4NO_3 down to -52° F but with considerable delay (ref. 3). Of the two, the dichloro compound gave the shorter delay. S,O-Ethylene chlorothiophosphite (2-chloro-1-thia-3-oxa-2-phospholane) was very hypergolic with WFNA (> 97 percent HNO_3) in an open-cup ignition test (refs. 3 and 18). It is an example of a cyclic halothiophosphite in which the sulfur is in the ring with phosphorus.

Amidothiophosphites: With respect to ignition reactivity, the most promising of all organophosphorus compounds is an amidothiophosphite. The substance, ethyl N,N,N',N'-tetramethyldiamidothiophosphite (bis-dimethylamido-ethyl-thiophosphite), gave a very low ignition delay of only 3 milliseconds at -70° F with both WFNA containing 4 percent

water and 4 percent sodium nitrite and a 1:1 blend of anhydrous WFNA and methane sulfonic acid (ref. 2). It also ignites readily with N_2O_4 and H_2O_2 (ref. 41). Its main disadvantage at the present time is its poor over-all yield (about 35 percent) on preparation (ref. 41). Contrary to expectations, the lower-molecular-weight homologue, methyl N,N,N',N'-tetramethyldiamidothiophosphite, had much longer delays with the WFNA-$NaNO_2$ oxidant as shown in the following table (ref. 41):

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Homologue	Ignition delay, millisec	
	-40° F	-70° F
Methyl	12	20
Ethyl	5	3

Physical properties. - Several alkyl thiophosphites meet many of the Bureau of Aeronautics target requirements and are, therefore, potentially attractive as major rocket fuels. Their boiling points are high, specific gravities are greater than unity, vapor pressures are low, and melting points are below -70° F with some mixtures fusing below -100° F (ref. 3). In addition, they remain quite fluid at low temperatures and are easily supercooled. Their disagreeable odors, however, constitute an annoying disadvantage. Other disadvantages are a decrease in hypergolicity and an increase in density and viscosity with air oxidation. Sensitivity to gum formation has also been reported (ref. 37).

Chemical properties. - Thiophosphites are not affected by water or steam at 212° F; however, hydrolysis may occur at higher temperatures (ref. 3). The thermal stability of some alkyl homologues is favorable even at about 400° F (refs. 3, 4, and 44). They can be stored without difficulty for long periods of time provided that atmospheric oxygen is excluded (ref. 3). In general, alkyl thiophosphites are about as toxic as aniline (refs. 3 and 26).

Economics. - Raw materials are available in sufficient quantities to exceed by far the requirements for 100 million pounds per year of thiophosphites (ref. 3). Cost calculations indicate that they can be manufactured to sell between 20 and 30 cents per pound based on an annual production of 15 million pounds per year. Large production can reduce the cost to a point that is less than that of rocket fuels currently used or considered for use (ref. 3).

The widening interest in alkyl thiophosphites resulted in a conference sponsored by the Air Force in Chicago on March 12, 1953, in which a discussion was held on the evaluation, production, and applications of these fuels (ref. 45).

Summary. - Of the few thiophosphites that have been investigated for rocket applications, triethyl trithiophosphite has probably been studied more extensively than any other organophosphorus compound. This and other low-molecular-weight alkyl thiophosphites are potentially attractive as major rocket fuels because they meet many of the Bureau of Aeronautics target requirements. They possess several disadvantages, however. Their ready oxidation in air is accompanied by a decrease in hypergolicity and increases in density and viscosity. Although they produce a clean, stable combustion, the exhaust gases are smoky and the combustion products are very corrosive, particularly in the nozzle section.

With respect to ignition delay, aryl thiophosphites, cyclic thiophosphites, and halothiophosphites are not as good as the low-molecular-weight alkyl esters. In contrast, the most promising of all organophosphorus compounds investigated to date is an amidothiophosphite with very low delays at low temperatures. Its main disadvantage at the present time is a poor over-all yield in preparation.

Phosphonites

General review. - Very little work has been done with esters of phosphonous acids as prospective rocket fuels. Even though only a few compounds have been investigated, they are distributed among several different subdivisions of this class (refs. 1, 20, 21, 22, and 24). A summary of ignition data obtained in an open-cup apparatus at room temperature and -40° F with several nitric acid oxidants is shown by table X. Although the results obtained with each particular compound are not necessarily representative of its category, a tentative order of decreasing ignition reactivity may be indicated as follows:

$$\text{halo} > \text{paraffinic} > \text{cyclic} > \text{olefinic} > \text{amido}$$

The position of the amidophosphonite may be attributed to its relatively large C_3 groups.

In another apparatus, the halo compound, benzenedichlorophosphonite, yielded delays with WFNA ($>$ 95 percent HNO_3) of about 35 and 110 milliseconds at 70° and -40° F, respectively (ref. 22). With the same acid, a 25 percent by volume blend of this phosphonite with 2-methyl-1-buten-3-yne gave a long delay of 355 milliseconds at room temperature (ref. 22) and no ignition at -40° F (ref. 1).

Summary. - Ignition-delay data from the few phosphonites that have been investigated indicate that this group of organophosphorus compounds is not as satisfactory a source of rocket fuels as several of the others already discussed.

Miscellaneous Organophosphorus Compounds

All compounds discussed in the preceding sections were synthesized and tested at least with respect to their ignition characteristics. There are a few compounds which cannot be classified conveniently in any of the foregoing categories or which have no information about them in rocket literature aside from some calculated performance data and estimated heats of formation. A summary of such data is shown in table XI.

Very few pentavalent organophosphorus compounds have ever been considered for use in propellant combinations. Some work with trialkyl tetrathiophosphates leads to a tentative conclusion that they have little practical value as rocket fuels (ref. 28).

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TABLE I. - TARGET REQUIREMENTS FOR ROCKET FUELS

FORMULATED BY BUREAU OF AERONAUTICS (REF. 1)

Density	Above 0.985 g/cc
Boiling point	Above 170° F
Melting point	Below -90° F
Viscosity	Free flowing at temperatures between -90° and 170° F
Toxicity	Relatively nontoxic
Physical state	Liquid desirable; however, gases with low vapor pressures are acceptable
Stability	Compounds should be resistant to chemical and thermal check, and should be stable during storage periods of six months to one year
Logistics	Compounds should be capable of being produced in tonnage quantities and at a cost of below 25 cents per pound
Ignition characteristics	Compounds should be easily ignitible (spark or spontaneous ignition) with such common oxidizers as liquid oxygen and fuming nitric acid
Specific impulse	Calculated values of above 270 lb-sec/lb with liquid oxygen or white fuming nitric acid are desirable
Materials of construction	Compounds should be compatible with such materials of construction as mild steel, aluminum, and their alloys

TABLE II. - SUMMARY OF IGNITION DATA FOR MIXED ALKYL THIOPHOSPHITES AND SEVERAL FUMING NITRIC ACIDS

[Small-scale rocket-engine apparatus]

Run	Average propellant temperature, °F	Initial pressure altitude, ft	Initial ambient pressure, mm Hg	Maximum combustion-chamber pressure, lb/sq in. gage	Time to attain maximum combustion-chamber pressure, sec	Water in oxidant, percent by weight	NO_2 in oxidant, percent by weight	Temperature, °F: Oxidant	Fuel	Injector head	Constant-temperature bath	Nozzle plate	Ambient air	Lead propellant into combustion chamber	Time between jet entries into combustion chamber, millisec	Ignition delay, millisec
Red fuming nitric acids																
244	120	90,000	12.9	205	0.4	3.6	19.4	120	120	122	122	70	81	Oxidant	4.8	5.3
334	120	82,500	18.5	(a)	(a)	2.7	19.8	120	121	123	123	65	87	Oxidant	26.7	5.7
245	120	0	760	220	.5	3.6	19.4	120	120	121	121	70	80	Fuel	14.3	3.4
246	81	0	760	218	0.7	3.6	19.4	81	81	81	81	81	74	Fuel	16.7	2.6
234	79	0	760	237	.7	3.6	19.4	79	79	79	79	77	86	Fuel	5.0	3.0
236	40	0	760	270	0.5	3.6	19.4	40	40	41	40	71	75	Fuel	7.5	3.2
247	2	0	760	225	0.4	3.6	19.4	1	2	2	1	69	70	Fuel	1.6	3.5
237	0	0	760	255	.3	3.6	19.4	0	0	2	0	55	60	Fuel	2.9	3.2
238	-39	0	760	242	0.3	3.6	19.4	-39	-39	-36	-37	56	57	Fuel	21.4	4.5
248	-39	0	760	220	.6	3.6	19.4	-39	-39	-38	-40	65	68	Fuel	2.3	3.5
252	-69	0	760	170	0.6	3.6	19.4	-69	-69	-68	-71	52	63	Oxidant	0.8	3.2
249	-79	0	760	160	0.3	3.6	19.4	-79	-79	-81	-80	50	59	Oxidant	1.0	3.7
250	-80	0	760	170	.6	3.6	19.4	-80	-80	-80	-81	52	59	Fuel	3.2	4.9
242	-91	0	760	220	0.3	3.6	19.4	-91	-91	-86	-89	52	68	Fuel	7.3	5.7
253	-93	90,000	12.9	(a)	(a)	3.6	19.4	-93	-93	-93	-93	45	64	Fuel	8.7	6.1
White fuming nitric acids																
340	121	0	760	295	0.5	1.9	0.7	120	121	121	121	82	75	Oxidant	26.1	5.6
262	118	76,600	24.5	157	.5	1.6	.3	118	119	118	118	48	79	Fuel	6.8	5.4
261	115	0	760	172	.5	1.6	.3	115	115	116	116	73	80	Oxidant	17.2	11.5
260	40	0	760	168	0.7	1.6	0.3	40	40	41	40	66	71	Oxidant	16.6	6.3
338	-39	0	760	208	.5	1.9	0.7	-39	-39	-41	-45	51	65	Oxidant	2.8	6.1

[a]No record.

TABLE III. - SUMMARY OF IGNITION DATA FOR TRIETHYL TRITHIOPHOSPHITE AND SEVERAL FUMING NITRIC ACIDS

[Small-scale rocket-engine apparatus]

Run	Average propellant temperature, °F	Initial pressure altitude, ft	Initial ambient pressure, mm Hg	Maximum combustion-chamber pressure, lb/sq in. gage	Time to attain maximum combustion-chamber pressure, sec	Water in oxidant, percent by weight	NO_2 in oxidant, percent by weight	Temperature, °F: Oxidant	Temperature, °F: Fuel	Temperature, °F: Injector head	Temperature, °F: Constant-temperature bath	Temperature, °F: Nozzle plate	Temperature, °F: Ambient air	Lead propellant into combustion chamber	Time between jet entries into combustion chamber, millisec	Ignition delay, millisec
Red fuming nitric acids																
341	121	90,000	12.9	290	0.5	2.7	19.8	121	121	121	119	63	84	Oxidant	3.7	4.1
258	121	0	760	220	.5	3.7	20.0	121	121	119	119	72	75	Oxidant	8.7	2.1
259	113	90,000	12.7	185	.7	3.7	20.0	113	113	115	115	71	86	Fuel	23.4	3.6
291	79	0	760	200	0.6	3.7	20.0	79	78	78	75	69	71	Oxidant	0.5	2.9
257	43	0	760	219	.7	3.7	20.0	43	43	45	45	68	72	Fuel	6.2	2.8
289	0	0	760	165	.5	3.7	20.0	0	--	1	0	58	49	Oxidant	4.5	3.8
254	-40	0	760	200	0.5	3.7	20.0	-40	-40	-38	-39	60	64	Oxidant	2.6	3.0
347	-70	90,000	12.9	245	0.7	2.7	19.8	-70	-70	---	---	53	67	Oxidant	10.2	6.2
290	-71	0	760	160	.7	3.7	20.0	-71	-71	-70	-73	46	62	Oxidant	[a]>4.6	5.7
255	-95	0	760	182	0.5	3.7	20.0	-94	-95	-94	-95	44	63	Fuel	4.1	4.9
256	-95	90,000	12.9	150	.5	3.7	20.0	-95	-95	-92	-92	44	61	Fuel	35.4	5.5
White fuming nitric acids																
335	122	90,000	12.9	282	0.5	1.9	0.7	121	122	123	123	53	62	Fuel	24.1	5.0
348	120	0	760	295	.6	.9	1.2	120	120	121	---	61	53	Oxidant	16.9	6.6
292	119	0	760	195	.4	1.6	.3	119	119	118	118	78	77	Fuel	16.3	5.3
266	40	0	760	146	0.7	1.6	0.3	40	40	41	41	64	70	Fuel	12.8	4.2
342	-39	90,000	12.9	278	0.6	1.9	0.7	-39	-39	-36	-40	55	61	Oxidant	34.0	5.8
293	-42	0	760	195	.7	1.6	.3	-42	-42	-39	-42	53	49	Fuel	16.5	5.3

[a]Exact value indeterminable because of fogged combustion chamber.

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TABLE IV. - SUMMARY OF IGNITION DATA FOR PROPYLENE N,N-DIMETHYLAMIDOPHOSPHITE AND SEVERAL FUMING NITRIC ACIDS

[Small-scale rocket-engine apparatus.]

Run	Average propellant temperature, °F	Initial pressure altitude, ft	Initial ambient pressure, mm Hg	Maximum combustion-chamber pressure, lb/sq in. gage	Time to attain maximum combustion-chamber pressure, sec	Water in oxidant, percent by weight	NO_2 in oxidant, percent by weight	Temperature, °F: Oxidant	Temperature, °F: Fuel	Temperature, °F: Injector head	Temperature, °F: Constant-temperature bath	Temperature, °F: Nozzle plate	Temperature, °F: Ambient air	Lead propellant into combustion chamber	Time between jet entries into combustion chamber, millisec	Ignition delay, millisec
Red fuming nitric acids																
278	132	0	760	208	0.8	3.7	20.0	132	132	133	133	78	80	Oxidant	2.9	1.7
277	120	0	760	197	.8	3.7	20.0	119	120	121	121	76	83	Fuel	13.4	1.3
337	119	90,000	12.9	288	.5	2.7	19.8	119	119	119	120	--	90	Fuel	12.9	2.6
281	100	0	760	205	.6	3.7	20.0	100	100	102	102	74	74	Oxidant	1.2	1.8
276	76	0	760	170	0.7	3.7	20.0	76	76	80	81	67	74	Fuel	15.2	1.8
280	62	0	760	193	.7	3.7	20.0	63	62	65	66	63	71	Fuel	15.4	2.0
275	42	0	760	182	.7	3.7	20.0	42	42	45	46	64	69	Oxidant	.9	2.3
279	22	0	760	200	.7	3.7	20.0	22	22	25	25	59	65	Oxidant	26.3	3.1
274	-1	0	760	170	0.7	3.7	20.0	-1	-1	-1	-1	64	65	Oxidant	24.4	2.8
286	-20	0	760	(a)	(a)	2.7	19.8	-20	---	-18	-20	57	59	Oxidant	26.1	4.1
273	-40	0	760	138	.7	3.7	20.0	-40	-39	-38	-40	49	66	Fuel	14.6	3.1
285	-55	0	760	170	.9	2.7	19.5	-56	-56	-54	-57	51	49	Oxidant	10.6	5.2
272	-72	0	760	125	0.7	3.7	20.0	-72	-71	-69	-70	36	66	(b)	(b)	5.7
271	-79	0	760	135	.8	3.7	20.0	-80	-78	-82	-86	39	70	Oxidant	(b)	9.1
283	-84	0	760	155	0.6	3.7	20.0	-84	-84	-81	-83	45	63	Oxidant	25.7	6.8
270	-87	0	760	114	.7	3.7	20.0	-87	-87	-84	-77	43	57	Fuel	12.6	7.0
344	-91	90,000	12.9	165	0.8	2.7	19.8	-91	-91	-90	-95	49	79	Oxidant	5.7	6.4
269	-93	0	760	100	.6	3.7	20.0	-93	-92	-91	-94	34	64	(b)	(b)	8.0
White fuming nitric acids																
333	139	0	760	235	0.5	1.9	0.7	139	139	140	141	81	81	Fuel	12.5	2.3
319	122	0	760	270	.5	1.9	.7	122	122	123	123	88	86	Oxidant	6.0	2.8
336	121	90,000	12.9	282	.5	1.9	.7	120	121	124	125	84	87	Fuel	16.5	2.8
332	119	0	760	288	.6	1.9	.7	120	119	121	121	88	86	Oxidant	2.4	2.6
331	83	0	760	288	0.6	1.9	0.7	82	83	87	82	77	77	Fuel	2.3	2.6
287	40	0	760	200	.5	1.6	.3	40	--	40	40	72	67	(c)	< .2	2.0
330	21	0	760	275	.7	1.9	.7	20	22	23	19	81	97	Oxidant	25.2	3.2
349	0	0	760	254	.5	.9	1.2	-1	1	0	0	73	79	Oxidant	30.2	3.3
328	-19	0	760	258	0.6	1.9	0.7	-20	-19	-17	-19	61	61	Fuel	3.9	3.5
346	-39	90,000	12.9	270	1.1	1.9	.7	-39	-39	-36	-44	55	67	Oxidant	35.0	5.2
288	-40	0	760	[d]155	[e].4	1.6	.3	-40	---	-39	-41	71	56	Oxidant	1.7	4.1

[a]No record obtained.
[b]Indeterminable because of frosted combustion chamber.
[c]Both propellants entered combustion chamber in same motion-picture frame.
[d]Peak pressure; maximum pressure possible was probably not attained.
[e]Time to attain peak combustion-chamber pressure.

TABLE V. - SUMMARY OF IGNITION DATA FOR NEAT AND BENZENE-DILUTED ALKYL PHOSPHINES WITH HYDROGEN PEROXIDES AT VARIOUS TEMPERATURES IN OPEN-CUP APPARATUS (REFS. 18 AND 19)

Phosphine	Class of phosphine	Amount of phosphine in blend, percent by volume	Amount of fuel used, ml	Amount of oxidant used, ml	Temperature, °F	Ignition delay
90-Percent hydrogen peroxide						
2-Ethylhexyl[a]	Primary	100	0.03	0.5	Ambient	Short[b]
		100	.06	.5	0	5 sec
		100	.14	.5	-20	4 sec
		40	.12	.5	Ambient	No ignition
		40	.16	.5	Ambient	2 sec
n-Octyl[c]	Primary	100	0.04	0.5	Ambient	Very short[d]
		100	.03	.5	Ambient	Short
		100	.08	.5	0	2 sec
		100	.12	.5	-20	Short
		50	.10	.5	Ambient	No ignition
		50	.15	.5	Ambient	Short
Dodecyl[e]	Primary	100	0.12	0.5	Ambient	No ignition
		100	.20	.5	Ambient	Short
Di-2-ethylhexyl[a]	Secondary	100	0.05	0.5	Ambient	1.4 sec
Tri-n-butyl	Tertiary	100	0.01	0.5	Ambient	Very short
		100	.06	.5	0	No ignition
		100	.08	.5	0	Very short
		100	.12	.5	-20	Short
		90	.20	.5	Ambient	No ignition
Tri-sec-butyl[f]	Tertiary	100	0.04	0.5	Ambient	Very short
		100	.08	.5	0	No ignition
		100	.10	.5	0	Short
		100	.14	.5	-20	Short
		90	.20	.5	Ambient	No ignition
Tri-2-ethylhexyl[a]	Tertiary	100	0.10	0.5	Ambient	No ignition
80-Percent hydrogen peroxide						
2-Ethylhexyl	Primary	100	0.06	0.5	Ambient	Short
		100	.06	.5	14	2 sec
		100	.08	.5	-22	15 sec
n-Octyl	Primary	100	0.06	0.5	Ambient	No ignition
		100	.08	.5	Ambient	Short
		100	.08	.5	14	Short
		100	.08	.5	-20	2 sec
Tri-n-butyl	Tertiary	100	0.06	0.5	Ambient	Short
		100	.12	.5	14	No ignition

[a]Prepared from phosphine and 2-ethylhexene.
[b]Short, noticeable delay but less than one second.
[c]Prepared from phosphine and 1-octene.
[d]Instantaneous to the senses.
[e]Prepared from phosphine and propylene tetramer.
[f]May have changed chemically since its preparation.

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TABLE VI. - SUMMARY OF IGNITION DATA FOR CYCLIC PHOSPHITES AND VARIOUS NITRIC ACID OXIDANTS AT ROOM TEMPERATURE AND AT -40° F IN OPEN-CUP APPARATUS

(REFS. 1, 21, 22, AND 24)

Cyclic Phosphite		Oxidant					
[a]Name	[b]Name	90-Percent WFNA		>95-Percent WFNA		Mixed acid	
		Room temperature	-40° F	Room temperature	-40° F	Room temperature	-40° F
Methylethylene phosphite	2-Methoxy-1,3,2-dioxaphospholane	---	---	[c]10+	[c]10	[c]10	[c]10
Butylethylene phosphite	2-Butoxy-1,3,2-dioxaphospholane	---	---	[d]8+	[d]8	[d]10	[d]9
Ethylpropylene phosphite	4-Methyl-2-ethoxy-1,3,2-dioxaphospholane	[e]9	[e]5	----	---	[e]10	[e]8
Propargylpropylene phosphite	4-Methyl-2-propargyloxy-1,3,2-dioxaphospholane	[f]10	[f]10	[d]10	[d]--	[f]10	[f]10
sym-2-Butynylenedi-propylene diphosphite	1,4-[bis(4-Methyl-1,3-dioxa-2-phospholyloxy)]-2-butyne	[f]10	[f]8	[c]10	[c]6	[f]10	[f]8
Ethyltrimethylene phosphite	2-Ethoxy-1,3,2-dioxaphosphorinane	---	---	[d]8-	[d]10	---	---

[a]Nomenclature according to ref. 15.
[b]Nomenclature according to indicated literature references.
[c]Reference 22.
[d]Reference 1.
[e]Reference 24.
[f]Reference 21.

Ignition rating scale	
Rating	Explanation
10	Violent flame - delay <1/2 sec
9	Good flame - delay <1/2 sec
8	Medium flame - delay <1/2 sec
7	Medium flame - delay <1 sec
6	Poor flame - delay >1 sec
5	Violent reaction - flames occasionally
4	Fast reaction - no flame
3	Medium reaction - no flame
2	Fair reaction - no flame
1	Poor reaction - no flame
0	No reaction

TABLE VII. - SUMMARY OF IGNITION DATA FOR AMIDOPHOSPHITES AND AMIDOHALOPHOSPHITES WITH HYDROGEN PEROXIDE AND SEVERAL NITRIC ACID OXIDANTS AT ROOM TEMPERATURE AND AT -40° F IN OPEN-CUP APPARATUS (REFS. 1, 22, AND 24)[a]

Fuel		Oxidant							
[b]Name	[c]Name	95 Percent WFNA		>98 Percent WFNA		Mixed acid		90 Percent H_2O_2	
		Room temperature	-40° F	Room temperature	-40° F	Room temperature	-40° F	Room temperature	-40° F
Acyclic amidophosphite									
Dibutyl N,N-diisopropylamidophosphite	Dibutyl diisopropylamido-phosphite	[illegible]	[illegible]	----	----	[illegible]	[illegible]	----	----
Cyclic amidophosphites									
Ethylene amidophosphite (polymer)	2-Amino-1,3,2-dioxaphospholane (polymer)	---	--	[illegible]	[illegible]	---	---	[illegible]	[illegible]
Ethylene N-methylamidophosphite	2-Methylamino-1,3,2-dioxaphospholane	---	--	[illegible]	[illegible]	---	---	[illegible]	[illegible]
Ethylene N,N-dimethylamidophosphite	2-Dimethylamino-1,3,2-dioxaphospholane	---	--	[illegible]	[illegible]	[illegible]	[illegible]	----	----
Ethylene N,N-di-n-butylamidophosphite	2-Di-n-butylamino-1,3,2-dioxaphospholane	---	--	[illegible]	[illegible]	---	---	[illegible]	[illegible]
Propylene N,N-dimethylamidophosphite	4-Methyl-2-dimethylamino-1,3,2-dioxaphospholane	---	--	[illegible]	[illegible]	---	---	[illegible]	[illegible]
Propylene N,N-diethylamidophosphite	4-Methyl-2-diethylamino-1,3,2-dioxaphospholane	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	----	----
Acyclic triamidophosphites[d]									
N,N,N',N'-Tetramethyltriamidophosphite	N,N,N',N'-Tetramethylphosphorous triamide	---	--	[illegible]	[illegible]	---	---	e,g10+	e,g10+
N,N,N',N',N",N"-Hexamethyltriamidophosphite	N,N,N',N',N",N"-Hexamethylphosphorous triamide	---	--	[illegible]	[illegible]	---	---	e,g10+	e,g10+
Acyclic amidohalophosphites									
N,N-Diisopropylamidodichlorophosphite	Diisopropylamidophosphorous dichloride	---	--	[illegible]	[illegible]	[illegible]	[illegible]	----	----
N,N,N',N'-Tetramethyldiamidochlorophosphite	N,N,N',N'-Tetramethylchlorophosphorous diamide	---	--	[illegible]	[illegible]	---	---	e,g10+	e,g10+
Cyclic amidodiphosphite									
Diethylene N-methylamidodiphosphite	N-Methyl-bis[2(-1,3,2-dioxaphospholanyl)] amine	---	--	[illegible]	[illegible]	---	---	[illegible]	[illegible]

[a]See table VI or ignition-rating scale.
[b]Nomenclature according to ref. 15 or extension of ref. 15.
[c]Nomenclature according to indicated literature references.
[d]Reference 24.
[e]Reference 1.
[f]Reference 22.
[g]Explosive reaction.

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TABLE VIII. - SUMMARY OF IGNITION-DELAY DATA FOR AMIDOPHOSPHITES AND AMIDOHALOPHOSPHITES WITH NITRIC ACID OXIDANTS AT VARIOUS TEMPERATURES IN OPEN-CUP APPARATUS

(REFS. 1, 4, 21, 22, 30, 31, AND 46)

Fuel		White fuming nitric acid, percent	Temperature, °F	Ignition delay, millisec	References
[a]Name	[b]Name				
Acyclic amidophosphite					
Dimethyl N,N-dimethylamidophosphite	Dimethylaminodimethylphosphite	>95	-40	[illegible]	25
Cyclic amidophosphites					
Ethylene N-methylamidophosphite	2-Methylamino-1,3,2-dioxaphospholane	>95	-40	6	1
Ethylene N,N-dimethylamidophosphite	2-Dimethylamino-1,3,2-dioxaphospholane	>95	70	[c]20	1,22
Ethylene N,N-dimethylamidophosphite	2-Dimethylamino-1,3,2-dioxaphospholane	>95	-40	11	1
Ethylene N,N-dimethylamidophosphite	2-Dimethylamino-1,3,2-dioxaphospholane	>95	-70	[c]30	1,22
Ethylene N,N-di-n-butylamidophosphite	2-Di-n-butylamino-1,3,2-dioxaphospholane	>95	-40	65	1
Propylene N,N-dimethylamidophosphite	4-Methyl-2-dimethylamino-1,3,2-dioxaphospholane	>95	75	15	4
Propylene N,N-dimethylamidophosphite	4-Methyl-2-dimethylamino-1,3,2-dioxaphospholane	>95	-40	15 - 21	1,4,30
Propylene N,N-dimethylamidophosphite	4-Methyl-2-dimethylamino-1,3,2-dioxaphospholane	>95	≈75	[d]10	4
Propylene N,N-dimethylamidophosphite	4-Methyl-2-dimethylamino-1,3,2-dioxaphospholane	99	75	5.3	46
Propylene N,N-diethylamidophosphite	4-Methyl-2-diethylamino-1,3,2-dioxaphospholane	90	70	[c]40	21
Propylene N,N-diethylamidophosphite	4-Methyl-2-diethylamino-1,3,2-dioxaphospholane	90	-65	[c]140	1
Ethylene N,N-tetramethyleneamidophosphite	2-Pyrrolidyl-1,3,2-dioxaphospholane	>95	-40	16	30,31
Propylene N,N-tetramethyleneamidophosphite	4-Methyl-2-pyrrolidyl-1,3,2-dioxaphospholane	>95	65	15	30
Propylene N,N-tetramethyleneamidophosphite	4-Methyl-2-pyrrolidyl-1,3,2-dioxaphospholane	>95	-40	17 - 18	4,30,31
Propylene N,N-tetramethyleneamidophosphite	4-Methyl-2-pyrrolidyl-1,3,2-dioxaphospholane	>95	-49	24	30
Propylene N,N-tetramethyleneamidophosphite	4-Methyl-2-pyrrolidyl-1,3,2-dioxaphospholane	90	68	19	30
Propylene N,N-tetramethyleneamidophosphite	4-Methyl-2-pyrrolidyl-1,3,2-dioxaphospholane	90	-40	25	30
Propylene N,N-tetramethyleneamidophosphite	4-Methyl-2-pyrrolidyl-1,3,2-dioxaphospholane	90	-76	29	30

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Acyclic triamidophosphites					
N,N',N"-Trimethyl-triamidophosphite	N,N',N"-Trimethyl-phosphorous triamide	>95	-40	15 - 16	4,30,31
N,N,N',N'-Tetramethyl-triamidophosphite	N,N,N',N'-Tetramethyl-phosphorous triamide	>95	68 to -58	≤12	1,4,30
N,N,N',N',N"-Pentamethyl-triamidophosphite	N,N,N',N',N"-Pentamethyl-phosphorous triamide	>95	-40	16	4,30,31
N,N,N',N',N",N"-Hexamethyl-triamidophosphite	N,N,N',N',N",N"-Hexamethyl-phosphorous triamide	>95	65 to -58	≤13	1,4,30
N,N,N',N',N",N"-Hexamethyl-triamidophosphite	N,N,N',N',N",N"-Hexamethyl-phosphorous triamide	>95	≈75	[e]10	4
Cyclic triamidophosphite					
N,N,N',N'-Tetramethyl-N",N"-tetramethylenetri-amidophosphite	N,N,N',N'-Tetramethyl-N",N"-tetramethylenephosphorous triamide	>95	68	10	30
N,N,N',N'-Tetramethyl-N",N"-tetramethylenetri-amidophosphite	N,N,N',N'-Tetramethyl-N",N"-tetramethylenephosphorous triamide	>95	-40	12 - 15	4,30,31
N,N,N',N'-Tetramethyl-N",N"-tetramethylenetri-amidophosphite	N,N,N',N'-Tetramethyl-N",N"-tetramethylenephosphorous triamide	90	68	12	30
N,N,N',N'-Tetramethyl-N",N"-tetramethylenetri-amidophosphite	N,N,N',N'-Tetramethyl-N",N"-tetramethylenephosphorous triamide	90	-40	24	30
N,N,N',N'-Tetramethyl-N",N"-tetramethylenetri-amidophosphite	N,N,N',N'-Tetramethyl-N",N"-tetramethylenephosphorous triamide	90	-76	36	30
Acyclic amidohalophosphites					
N,N-Dimethylamido-dichlorophosphite	N,N-Dimethyldichloro-phosphorous amide	>95	-40	26	30,31
N,N,N'-Trimethyldiamido-chlorophosphite	N,N,N'-Trimethylchloro-phosphorous diamide	>95	-40	21	30
N,N,N',N'-Tetramethyl-diamidochlorophosphite	N,N,N',N'-Tetramethylchloro-phosphorous diamide	>95	-40	10	1
Cyclic amidodiphosphite					
Diethylene N-methyl-amidodiphosphite	N-Methyl-bis[2(1,3,2-dioxaphospholanyl)]amine	>95	-40	10	1

[a]Nomenclature according to ref. 15 or extension of ref. 15.
[b]Nomenclature according to indicated literature references.
[c]Approximate value.
[d]Impinging jets with splash plate.
[e]Impinging jets with no splash plate.

TABLE IX. - SUMMARY OF IGNITION-DELAY DATA FOR TRIMETHYL TRITHIOPHOSPHITE - UNSATURATED HYDROCARBON BLENDS AND RED FUMING NITRIC ACID CONTAINING 22.6 PERCENT NO_2 AND 0.99 PERCENT H_2O AT -40° AND -65° F IN OPEN-CUP APPARATUS 3110

(REF. 29)

Hydrocarbon	Temperature, °F	Ignition delay, millisec				
		Amount of hydrocarbon, percent by volume				
		0	20	40	60	80
2-Methyl-1-pentene	-40	10.0	17.6	20.1	59.6	(a)
	-65	13.0	10.4	15.8	114	(a)
1-Hexene	-40		8.2	19.1	41.8	(a)
	-65		12.8	17.5	34.9	
Isoprene	-40		3.3	18.0	19.6	51.3
	-65		11.6	31.8	44.6	135
Dipentene	-40		8.8	12.4	90.5	406
	-65		11.0	14.9	139	(a)
1-Vinyl-3-cyclohexene	-40		8.5	11.9	59.1	(a)
	-65		8.8	16.6	89.0	
Styrene	-40		7.8	13.3	68.8	818
	-65		16.4	15.1	73.5	(a)
Phenylacetylene	-40		12.8	5.3	400	135
	-65		(a)	(a)	(a)	(a)

[a]No ignition.

TABLE X. - SUMMARY OF IGNITION DATA FOR SEVERAL PHOSPHONITES AND VARIOUS NITRIC ACID OXIDANTS AT ROOM TEMPERATURE AND AT -40° F OBTAINED IN OPEN-CUP APPARATUS (REFS. 20, 21, 22, AND 24)

Fuel		[a]Oxidant					
[b]Name	[c]Name	90-Percent WFNA		>95-Percent WFNA		Mixed acid	
		Room temper-ature	-40° F	Room temper-ature	-40° F	Room temper-ature	-40° F
Paraffinic phosphonite							
Dimethyl benzene-phosphonite	Dimethyl benzene-phosphonite	[d]10	[d]1	[e]10	[e]10	[d]10	[d]0
Olefinic phosphonite							
Diallyl benzene-phosphonite	Diallyl benzene-phosphonite	[f]4	--	----	---	----	---
Cyclic phosphonite							
Propylene methane-phosphonite	2,4-Dimethyl-1,3,2-dioxaphospholane	[d]9	[d]8	----	---	[d]8	[d]9
Halophosphonite							
Benzenedichloro-phosphonite	Benzenephosphonous dichloride	---	--	[e]10+	[e]10	[e]10+	[e]10
Amidophosphonite							
N,N,N',N'-Tetra-isopropyl-benzenediamido-phosphonite	N,N,N',N'-Tetraiso-propyl benzene-phosphonousdiamide	[g]2	(g)	----	---	[g]4	(g)

[a]See table VI for ignition-rating scale.

[b]Nomenclature according to ref. 15 or extension of ref. 15.

[c]Nomenclature according to indicated literature references.

[d]Ref. 21.

[e]Ref. 22.

[f]Ref. 20.

[g]Ref. 24.

TABLE XI. - SUMMARY OF CALCULATED PERFORMANCE DATA AND ESTIMATED HEATS OF FORMATION FOR SEVERAL ORGANOPHOSPHORUS COMPOUNDS WITH LIQUID OXYGEN (REF. 4)

[a]Fuel	[b]Fuel	Oxidant-fuel weight ratio (c)	Chamber temperature, °K	Average molecular weight in chamber	Specific impulse, lb-sec/lb		Characteristic velocity, ft/sec	Altitude index, miles (d)	Estimated heat of formation, kcal/mole
					Frozen	Equilibrium			
N,N-Tetramethylene-N',N"-ethylenetriamidophosphite	2-Pyrrolidyl-1,3,2-diaza-phospholane	1.31	3290	22.3	243	250	5500	455	25
N,N-Dimethyl-N',N"-ethylene-triamidophosphite	2-Dimethylamino-1,3,2-diaza-phospholane	1.20	3280	22.8	243	250	5500	455	31
N,N,N',N"-Diethylene-triamidophosphite	2-Ethyleneimino-1,3,2-diaza-phospholane	1.10	3310	23.6	243	251	5500	459	0
Dimethylphosphinamide	Dimethylaminophosphine	1.25	3380	22.4	245	255	5650	474	15
Phosphinamide	Aminophosphine	.65	3190	25.5	226	235	5180	388	19

[a]Nomenclature according to ref. 15 or extension of ref. 15.

[b]Nomenclature according to indicated literature reference.

[c]Mixture ratio chosen for combustion to CO and H_2O.

[d]Altitude attained by a "standard" rocket in vertical flight assuming no friction and optimum design of the propellant tanks for the chosen densities (see ref. 1). Average propellant density assumed to be 1 g/cc.

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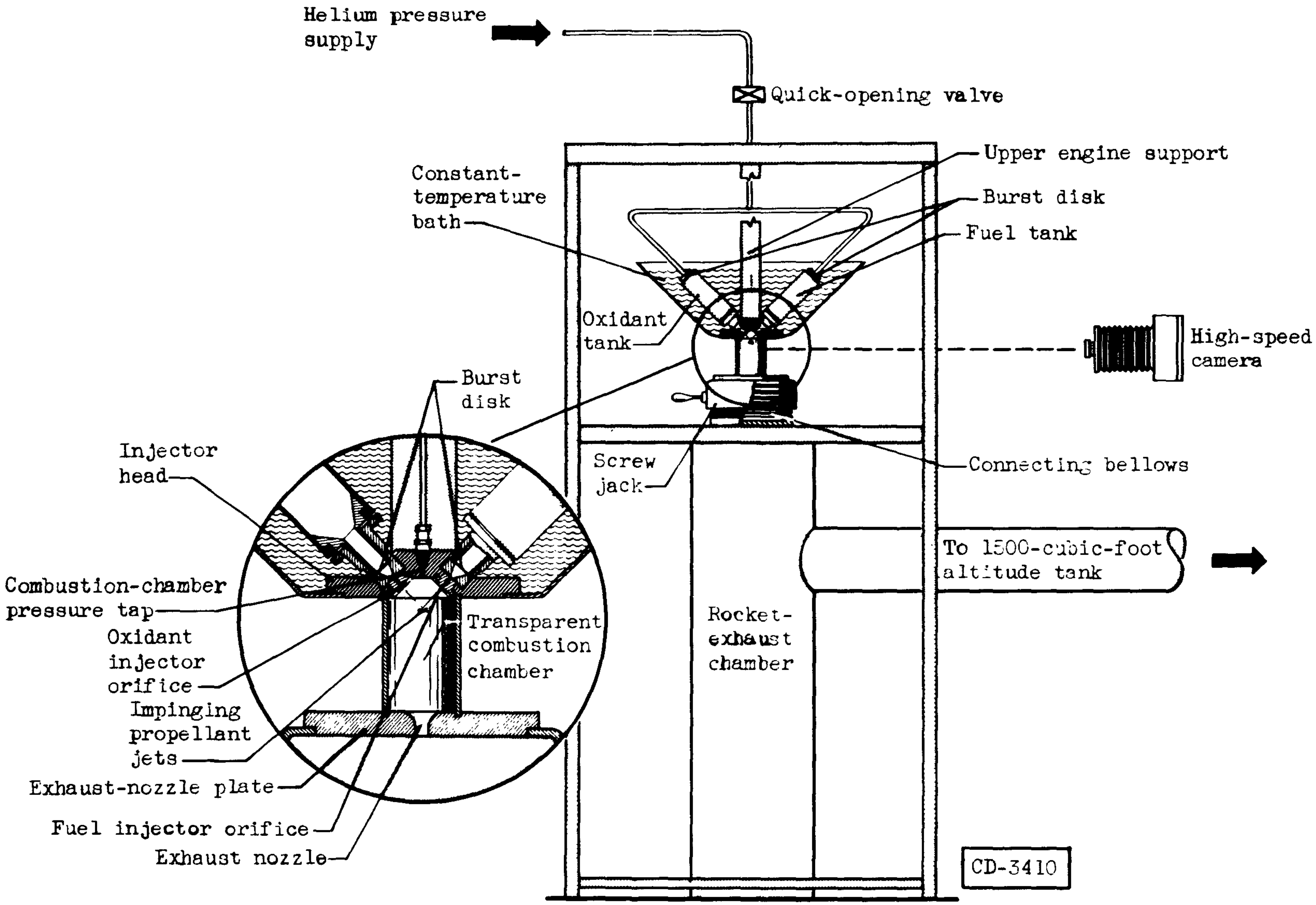

Figure 1. - Diagrammatic sketch of small-scale rocket-engine ignition-delay apparatus.

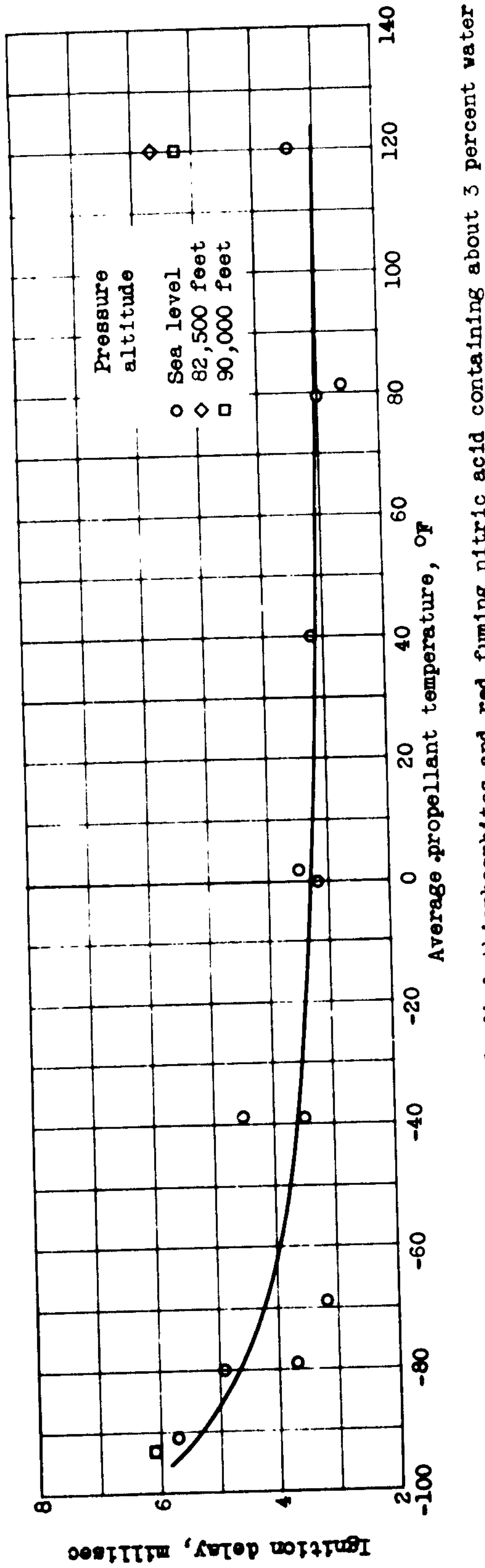

Figure 2. - Ignition delay of mixed alkyl thiophosphites and red fuming nitric acid containing about 3 percent water and 19 to 20 percent nitrogen dioxide by weight.

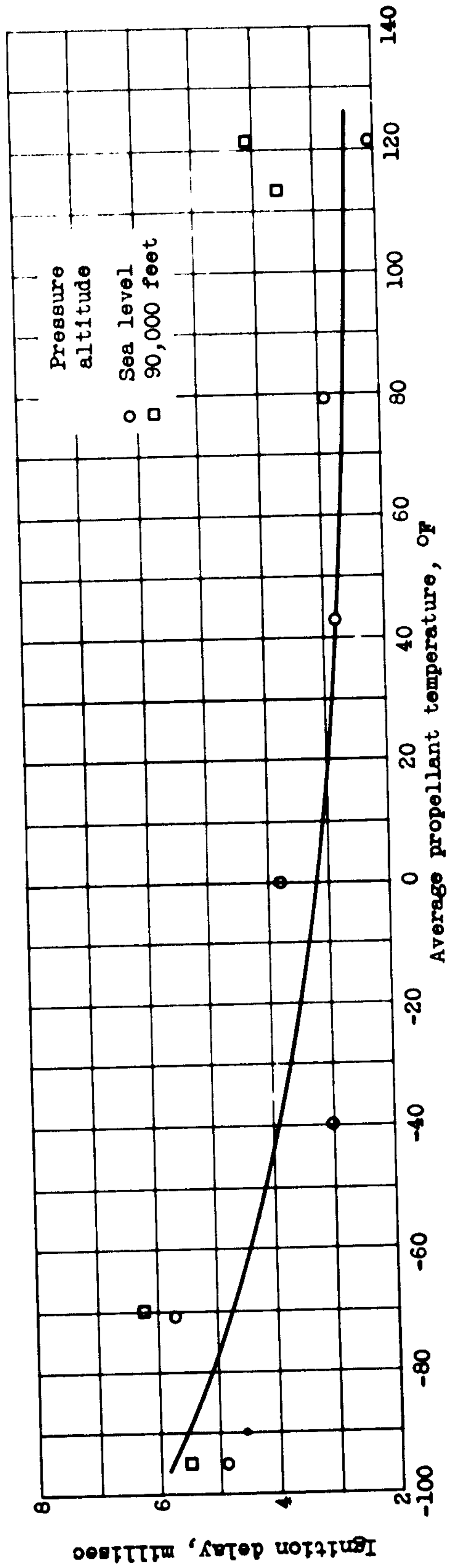

Figure 3. - Ignition delay of triethyl trithiophosphite and red fuming nitric acid containing 3 to 4 percent water and 20 percent nitrogen dioxide by weight.

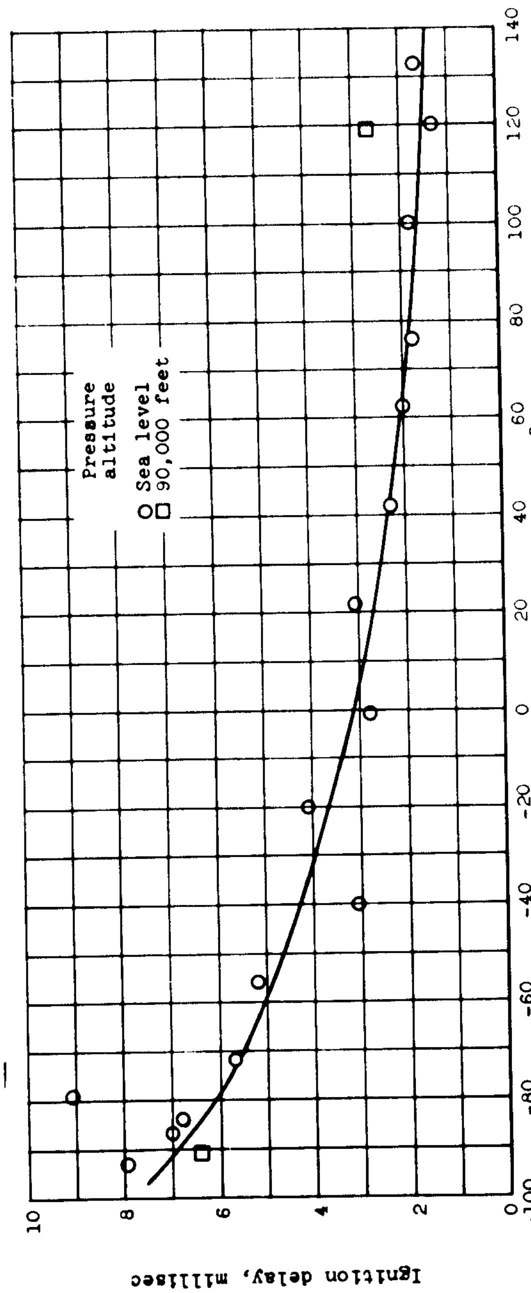

Figure 4. - Ignition delay of propylene N,N-dimethylamidophosphite and red fuming nitric acid containing about 3 percent water and 20 percent nitrogen dioxide by weight.

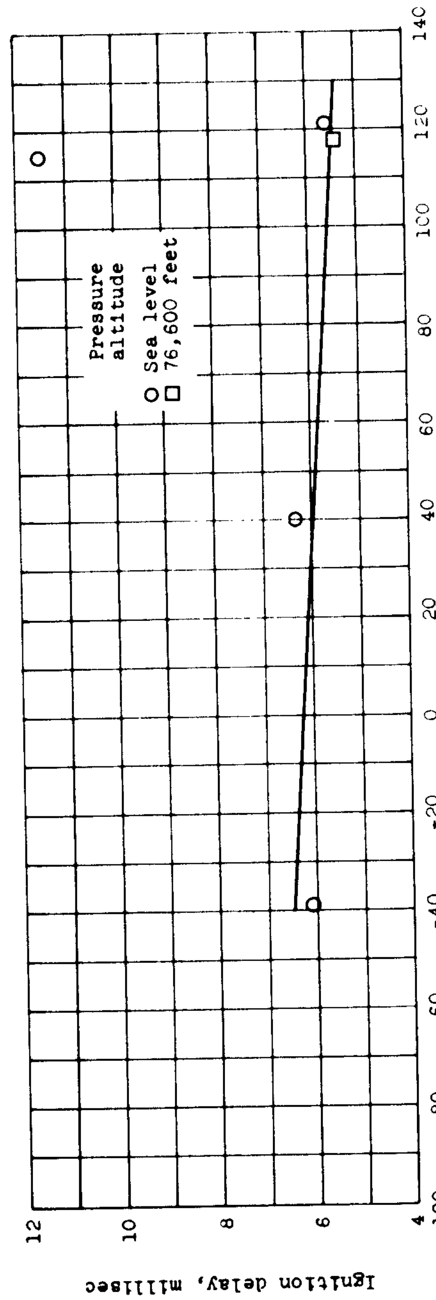

Figure 5. - Ignition delay of mixed alkyl thiophosphites and white fuming nitric acid (USAF Specification No. 14104).

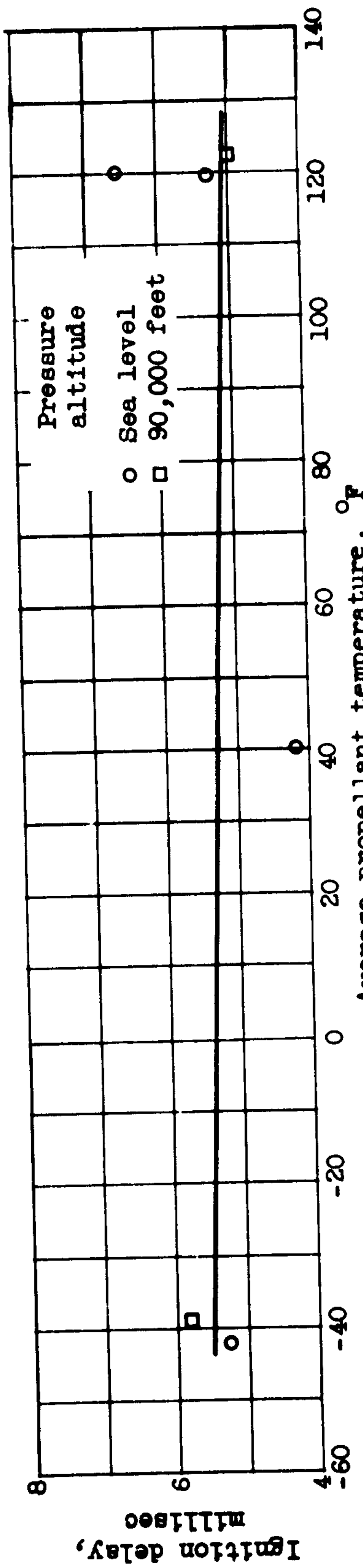

Figure 6. - Ignition delay of triethyl trithiophosphite and white fuming nitric acid (USAF Specification No. 14104).

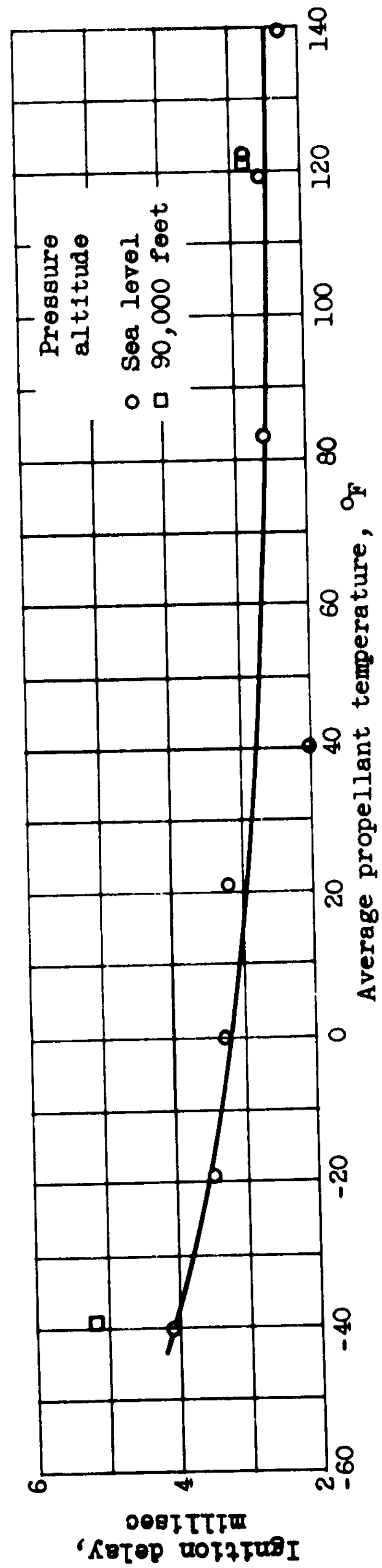

Figure 7. - Ignition delay of propylene N,N-dimethylamidophosphite and white fuming nitric acid (USAF Specification No. 14104).

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ORGANOPHOSPHORUS COMPOUNDS IN ROCKET-ENGINE APPLICATIONS. Dezso J. Ladanyi and Glen Hennings. April 1954. (ii), 52p. diagrs., 11 tabs. (NACA RM E54A26) CONFIDENTIAL

Experimental ignition-delay determinations of mixed alkyl thiophosphites, triethyl trithiophosphite, and propylene N,N-dimethylamidophosphite with red and white fuming nitric acids were conducted at temperatures from 140° to -95° F at sea-level pressure and at pressure altitudes of about 90,000 feet with a small-scale rocket engine of approximately 50 pounds thrust. Regardless of propellant combination or imposed temperature and pressure conditions, the ignition delays were all less than 10 milliseconds; most were in the range 1 to 6 milliseconds. In addition, the literature pertaining to the use of organophosphorous compounds in rocket-propellant combinations was surveyed and summarized with particular emphasis on ignition-delay investigations.
Copies obtainable from NACA, Washington

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1. Engines, Rocket (3.1.8)
2. Fuels - Properties, Physical and Chemical (3.4.2)
3. Fuels - Relation to Engine Performance(3.4.3)
4. Fuels - Rockets (Includes Fuel and Oxidant) (3.4.3.3)
5. Combustion - Rocket Engines (3.5.2.5)

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4. Fuels - Rockets (Includes Fuel and Oxidant) (3.4.3.3)
5. Combustion - Rocket Engines (3.5.2.5)

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ORGANOPHOSPHORUS COMPOUNDS IN ROCKET-ENGINE APPLICATIONS. Dezso J. Ladanyi and Glen Hennings. April 1954. (ii), 52p. diagrs., 11 tabs. (NACA RM E54A26) CONFIDENTIAL

Experimental ignition-delay determinations of mixed alkyl thiophosphites, triethyl trithiophosphite, and propylene N,N-dimethylamidophosphite with red and white fuming nitric acids were conducted at temperatures from 140° to -95° F at sea-level pressure and at pressure altitudes of about 90,000 feet with a small-scale rocket engine of approximately 50 pounds thrust. Regardless of propellant combination or imposed temperature and pressure conditions, the ignition delays were all less than 10 milliseconds; most were in the range 1 to 6 milliseconds. In addition, the literature pertaining to the use of organophosphorous compounds in rocket-propellant combinations was surveyed and summarized with particular emphasis on ignition-delay investigations.
Copies obtainable from NACA, Washington

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1. Engines, Rocket (3.1.8)
2. Fuels - Properties, Physical and Chemical (3.4.2)
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